A

# HAND-BOOK

OF

# INDUSTRIAL ORGANIC CHEMISTRY

ADAPTED FOR THE USE OF

MANUFACTURERS, CHEMISTS, AND ALL INTERESTED IN THE UTILIZATION OF ORGANIC MATERIALS IN THE INDUSTRIAL ARTS.

BY

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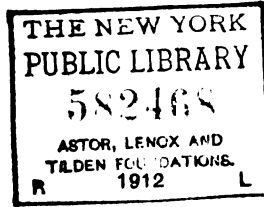
# PREFACE TO THE THIRD EDITION.

THE subject of Industrial Organic Chemistry covers such a wide range of topics and considers the utilization of such a variety of raw materials of both animal and vegetable origin, and the production of such a multitude of useful and valuable substances, that a thorough survey of the ground is a laborious undertaking. Nevertheless, the lapse of five years since the appearance of the previous edition of this work makes such a survey necessary, as notable advances have been made in many of the chemical industries during that time.

Every chapter, therefore, has been revised and new matter added, while older and less important portions have been stricken out. The chapters on Natural and Artificial Dye-colors have been largely rewritten, because of the rapid progress in discovery in these lines during the last few years. It has been sought to incorporate in the book all of this advance in our knowledge that is definitely accepted by chemists. Several new tabular statements have also been incorporated in these chapters, which it is hoped will prove of value.

The chapters on Fatty Oils, Essential Oils, Fermentation, Tanning, Textile Fibres, and Destructive Distillation have had important additions made to them.

The Bibliography has in all chapters been brought down to date, and the Statistics are the most recent attainable. The author desires to acknowledge his indebtedness to numerous friends and correspondents for items of valuable information not readily accessible.

American chemical industry has advanced with rapid strides in recent years, and the need of a thorough understanding of the chemical character and possibilities of materials is becoming every day better appreciated by our manufacturers as a class. The author hopes that the book may continue to serve, as it has already served in the past, in bringing about this desirable consummation.

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PHILADELPHIA, October, 1900.

# PREFACE TO THE FIRST EDITION.

THE literature of Applied Chemistry is reasonably voluminous. We have dictionaries and encyclopædic works upon the subject, a series of small hand-books for individual industries, and a mass of technical journals of both general and special application. Works, however, in which the effort is made to give within the bounds of a single volume a general view of the various industries based upon the applications of chemistry to the arts are much rarer, and especially is this true of works printed in the English language. In German we have Wagner's "Chemische Technologie," brought down to date by its present editor, Ferd. Fischer; Post's "Chemische Technologie," Bolley's "Technische-Chemische Untersuchungen," Heinzerling's "Technische Chemie," Ost's "Chemische Technologie," and others; in French, Payen's "Chimie Industrielle" and Girardin's "Chimie appliqué aux Arts Industriels," etc.; while in English we have only the now antiquated translations of Wagner and Payen. In speaking thus, the writer wishes to be understood as referring only to general works on chemical technology of moderate size. The excellent "Dictionary of Applied Chemistry," in three volumes, now being published by Longmans & Co., does not therefore come into the consideration, for the twofold reason of its size and of its encyclopædic and disconnected method of treatment.

Similarly, works which cover only a single side of the subject, like Allen's "Commercial Organic Analysis," are not referred to in the above statement.

The author has endeavored within the compass of a moderate-sized octavo to take up a number of the more important chemical industries or groups of related industries, and to show in language capable of being understood even by those not specially trained in chemistry the existing conditions of those industries. The present volume, it will be noticed, is limited to "Industrial Organic Chemistry." This field, while covering many very important lines of manufacture, does not seem at present to be so well provided for as the inorganic part of the subject. A companion volume, covering this other side of industrial chemistry, is in contemplation.

In taking up the several industries for survey, it has been thought desirable first to enumerate and describe the raw materials which serve as the basis of the industrial treatment; second, the processes of manufacture are given in outline and explained; third, the products, both intermediate and final, are characterized and their composition illustrated in many cases by tables of analyses; fourth, the most important analytical tests and methods

are given, which seem to be of value either in the control of the processes of manufacture or in determining the purity of the product; and, fifth, the bibliography and statistics of each industry are given, so that an idea of the present development and relative importance of the industry may be had.

The author has endeavored in a number of cases to give a clearer picture of the lines of treatment for an industry by the introduction of schematic views of the several processes through which the raw material is carried until it is brought out as the finished product. A number of these diagrams have been taken from German and English sources, and several have been constructed by the author specially for this work. A list of these diagrams will be found appended.

A large number of the illustrations have been drawn specially for this work, and others have been procured from the best German and American sources.

Frequent foot references are made to authorities and sources of information, although this may not have been done in all cases. The author has in the analytical section made frequent use of Allen's "Commercial Organic Analysis," and hereby desires to acknowledge his special indebtedness to that most valuable work. He has also made frequent use of Wagner's "Chemische Technologie," thirteenth edition, and Stohmann and Kerl's "Angewandte Chemie." Besides these works of a general character he has also consulted a large number of special works, the titles of which will be found in the bibliographical lists appended to each chapter.

The author desires here to acknowledge his indebtedness to the many friends who have aided him by information and helped him especially in the collating of the statistics of the several industries.

His special indebtedness is due to his friend and former pupil, Mr. Louis J. Matos, M.E., who aided him in the completion of Chapters XI. and XII., and to whom Chapter XIV. in its entirety belongs.

To his colleague, Professor Henry Trimble, of the Philadelphia College of Pharmacy, he is also indebted for information upon the subject of Tannin and Dye-woods, as treated in Chapter XIII.

The original drawings made for this work and the index are also due to Mr. L. J. Matos.

The author hopes that this work may prove of some value to those engaged in the several lines of manufacturing industry touched upon by showing the chemical nature of the materials which are handled by them, and of the change which these materials undergo in the course of treatment and preparation as marketable commodities; that it may be suggestive to those engaged in research or invention in connection with chemistry; and, lastly, that it may be found to possess some interest for the general reader or the student of scientific or economic topics.

PHILADELPHIA, August 3, 1891.

# PREFACE TO THE SECOND EDITION.

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THE fact that a large edition of this work has been exhausted in about three and one-half years, and that the book has been temporarily out of print, leads the author to believe that the plan of treatment adopted in the book was an acceptable one, and that such a book was needed. While some of the author's correspondents have referred to the very condensed treatment which some of the industries necessarily received, others have recognized that this feature particularly commended it as a convenient hand-book, or as a text-book for students. For those who wish the fullest information on particular subjects the Bibliography will go far towards indicating the sources for its supply. Were it not for the great range of scientific periodicals through which new communications are scattered, the journal literature might also be cited. In a German translation of the work, which has appeared recently, by Dr. J. Ephraim, published by Jos. Ambrosius Barth, Leipzig, this reference to the journal literature has been attempted and partially carried through. The author, however, has not taken it up for the reason stated.

In the present edition the Bibliography has in all cases been rewritten and brought carefully to date. The Statistics have also been brought down to the present year whenever new figures were attainable, and a number of new statistical tables have been added.

While the body of the text has not been altered, numerous corrections have been made and new sections inserted in many cases.

In the Appendix two new tables have been added giving the physical and chemical constants of the oils, fats, and waxes, classified for reference and comparison.

The author desires to acknowledge his indebtedness to many friends for kind suggestions, and in especial to Mr. Louis J. Matos, who supplied information in connection with the last three chapters, and to Mr. Samuel S. Sadtler, who aided in gathering statistics and in reading proofs.

Hoping that the book will again meet the public approval and prove useful and suggestive to those interested, the author submits this new edition.

PHILADELPHIA, August, 1895.

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# INDUSTRIAL ORGANIC CHEMISTRY.

## CHAPTER I.

### PETROLEUM AND MINERAL OIL INDUSTRY.

### I. Raw Materials.

THE raw materials of this industry are hydrocarbons and products derived from them by alteration, which occur associated together in nature. They may be gaseous, liquid, or solid, and very frequently all three of these physical modifications are found admixed in the same crude material. As, on the other hand, they occur at times separate and distinct, they will be separately noted.

1. NATURAL GAS.—Under this name is generally known now the mixture of inflammable gases that is found issuing from the earth in various localities. While it is chiefly in connection with the boring of wells for oil or salt, or as a constantly-forming product of decomposition in coal-mines, that it has been obtained, we find that it often occurs entirely independently of these. "Burning springs," as they have been termed, have been known from the earliest historical times. Those of Baku, on the Caspian Sea, are supposed to have been burning as early as the sixth century before Christ, and to have been a sacred shrine of the Persian fire-worshippers. The Chinese have employed natural gas for centuries in their salt-mines as a source of illumination. In the United States it was employed already in 1821, at Fredonia, New York, as a source of illumination, and for fifty years past has served as the fuel for the evaporation of brine at the salt-wells of the Kanawha Valley, West Virginia.

In chemical composition, natural gas is relatively uniform. It consists essentially of methane (marsh-gas), the first member of the paraffin series of hydrocarbons, which may be accompanied by ethane, propane, and the members of the paraffin series next following methane. Small quantities of hydrogen, carbon monoxide, and dioxide have been found to be present at times, while nitrogen is apparently an invariable impurity. The following table gives the results of analyses of natural gases, made in 1886, by Prof. F. C. Phillips for the Second Geological Survey of Pennsylvania. The localities chosen are all in Western Pennsylvania, with the exception of Fredonia, New York, which is introduced because of its historical interest:

| CONSTITUENTS. | Fredonia, New York. | Sheffield, Warren Co., Pa. | Wilcox, McKean Co., Pa. | Kane, McKean Co., Pa. | Speechley, near Oil City, Pa. | Lyon's Run, Murrysville, Pa. | Raccoon Creek, Beaver Co., Pa. | Baden, Beaver Co., Pa. | Houston, near Cannonsburg, Pa. |
|---|---|---|---|---|---|---|---|---|---|
| Paraffin hydrocarbons | 90.05 | 90.64 | 90.38 | 90.01 | 95.42 | 97.70 | 90.09 | 87.27 | 84.26 |
| Olefine hydrocarbons | . . . | . . . | . . . | . . . | . . . | . . . | . . . | . . . | . . . |
| Carbon dioxide . . . | 0.41 | 0.30 | 0.21 | 0.20 | 0.05 | 0.20 | Trace. | 0.41 | 0.44 |
| Hydrogen . . . . . | . . . | . . . | . . . | . . . | 0.02 | . . . | . . . | . . . | . . . |
| Oxygen . . . . . . | Trace. | Trace. | Trace. | Trace. | Trace. | Trace. | Trace. | Trace. | Trace. |
| Nitrogen . . . . . | 9.54 | 9.06 | 9.41 | 9.79 | 4.51 | 2.02 | 9.91 | 12.32 | 15.30 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

The paraffins contained in these gases have the following composition by weight:

| | Fredonia, New York. | Sheffield, Warren Co., Pa. | Wilcox, McKean Co., Pa. | Kane, McKean Co., Pa. | Speechley, near Oil City, Pa. | Lyon's Run, Murrysville, Pa. | Raccoon Creek, Beaver Co., Pa. | Baden, Beaver Co., Pa. | Houston, near Cannonsburg, Pa. |
|---|---|---|---|---|---|---|---|---|---|
| Carbon . . . . . . | 78.14 | 76.69 | 76.52 | 76.77 | 77.11 | 74.96 | 76.42 | 76.48 | 76.68 |
| Hydrogen . . . . . | 21.86 | 23.31 | 23.48 | 23.23 | 22.89 | 25.04 | 23.58 | 23.52 | 23.32 |
| | 100.00 | 100.00 | 100.00 | 100 00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

With these may be compared the natural gas from two important petroleum-yielding localities in Europe, viz., Pechelbronn, in Alsace, and Baku, on the Caspian.

| | Pechelbronn I. (Engler.) | Pechelbronn II. (Engler.) | Pechelbronn III. (Engler.) | Baku I. (Schmidt.) | Baku II. (Schmidt.) |
|---|---|---|---|---|---|
| Methane . . . . | 78.6 | 68.2 | 77.3 | 92.49 | 93.09 |
| Olefines . . . . | 4.0 | 3.4 | 4.8 | 4.11 | 3.26 |
| Carbon dioxide . | 2.2 | 2.9 | 3.6 | 0.93 | 2.18 |
| Carbon monoxide | 3.0 | 3.7 | 3.4 | . . | . . |
| Hydrogen . . . | . . | . . | . . | 0.34 | 0.98 |
| Oxygen . . . . | . . | 4.3 | 2.0 | . . | . . |
| Nitrogen . . . . | 17.2 | 16.9 | 9.0 | 2.13 | 0.49 |
| | 100.00 | 99.6 | 100.10 | 100.00 | 100.00 |

2. CRUDE PETROLEUM (syn. *Erdoel, Naphtha,* etc.).—Under this heading is included the liquid product which is obtained so abundantly in various parts of the earth, either issuing from the ground naturally or gotten by the boring of wells through the overlaying rocks to the oil-bearing strata. The oldest and so far the most important petroleum district of the world is the Appalachian field of Western Pennsylvania, extending from Alleghany County, New York, through Pennsylvania, southwesterly into West Virginia and Eastern Ohio. While the oils found in this district may differ considerably in gravity, color, and undoubtedly in chemical composition, the differences are not fundamental, and with certain special exceptions the crude oils from various localities are all brought together by

the pipe-lines and become mixed before going to the refineries. None of these Pennsylvania or West Virginia oils contain any appreciable amount of sulphur or other impurity which would require a modification of the general refining methods. The heavy oils of Franklin and Smith's Ferry, Pennsylvania, and some few other localities are so valuable for the manufacture of lubricating oils that they are collected and worked separately. The Pennsylvania crude oil has in general a dark greenish-black color, appearing claret-red by transmitted light, and varies ordinarily in specific gravity from 0.782 to 0.850, or, as it is frequently expressed, from 49° B. to 34° B. Exceptions to this are the Washington County amber oil, the light-colored Smith's Ferry oil, and some other natural yellow or amber oils. In chemical composition it is essentially composed of hydrocarbons of the paraffin series $C_nH_{2n+2}$, the gaseous and the solid members of the series being alike held dissolved in the liquid ones, and smaller amounts of the hydrocarbons of the olefine series $C_nH_{2n}$, and the benzene series $C_nH_{2n-6}$. According to Markownikoff, Pennsylvania petroleum also contains hydrocarbons of a series, $C_nH_{2n}$, which he terms "naphthenes," which are probably hydrogen addition compounds of the aromatic series. Within recent years another important field has developed, viz., Ohio, which includes the two distinct districts, the Lima oil district and the Macksburg district. The former is by far the more important, but the product is peculiar in that it contains sulphur, and has an offensive odor similar to Canadian crude oil. Careful analyses made in the author's laboratory have shown that it contains on an average 0.42 per cent. of sulphur, combined in relatively stable forms not decomposed by simple distillation.* Reference will be made to it in speaking of refining methods. Within recent years the extension of the Lima (or Trenton Limestone) oil-field westerly into Indiana has added to the production of this grade of oil. The most important localities in the United States, outside of the Pennsylvania and Ohio oil-fields, are Texas, Colorado, and California, in which latter State a blackish petroleum of rather heavier consistency than Pennsylvania petroleum is found quite abundantly. This California petroleum is peculiar in containing nitrogenous bases of the pyridine and quinoline groups, and in leaving, instead of paraffine, an asphaltic base or residuum.

Closely related to the Pennsylvania and New York oil-fields is the oil district of Canada. This is in the neighborhood of Enniskillen, in the western section of the province of Ontario. The Canadian petroleum, however, is distinctly different from that of Pennsylvania. It is darker in color, heavier in gravity, and is of a very offensive odor on account of sulphur impurity, and is therefore more difficult and expensive to refine. As before stated, it finds a counterpart in the oil of Lima, Ohio.

Second in importance to the Pennsylvania oil-fields, and even more prolific in the yield of individual wells, is the Russian petroleum district of Baku, on the Caspian. For detailed accounts of the extraordinary production of these wells, the reader is referred to Boverton Redwood's "Petroleum and its Products," vol. i. p. 26, or to Engler's articles in Dingler's *Polytechnisches Journal*, Bd. cclx and cclxi. The Russian petroleum has a higher gravity than the American, averaging 0.873, or 31° B., and has been found to be entirely different in its chemical composition, consist-

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* Mabery (*Am. Chem. Jour.*, April, 1891) has identified in Ohio petroleum methyl, ethyl, normal propyl, iso- and normal butyl, pentyl, ethyl-pentyl, and hexyl sulphides.

ing for the most part of hydrocarbons of the series $C_nH_{2n}$, isomeric with the olefine series, and called "naphthenes." As will be seen later, this difference in chemical composition involves a difference in the refining results.

The most important of the other European petroleum-fields are those of Galicia, which produce a variety of oils, both light and heavy, either accompanying or independent of the ozokerite of the region, those of Hanover, which yield thick oils, varying in specific gravity from .862 to .910, and those of Alsace, which also yield oils predominantly heavy, and used chiefly for lubricants.

The Asiatic petroleum-fields are those of Burmah, which have long been known to be very rich, and which, under British control, will now be developed, and those of Rangoon, in India, the oils from which are thick and heavy, yielding much lubricating oil and paraffin, and those of Japan.

3. CRUDE PARAFFINE.—Under this head may be understood the more or less compact solid material which often accompanies crude petroleum, is deposited from it on standing, and in some cases is found in extensive deposits independently of it. Thus, a deposit of buttery consistency separates from some crude oils, such as Bradford oil, and adheres to the pumping machinery and derrick, forming a crust which has to be scraped off from time to time. The same oils deposit crude paraffine in the pipe-lines, necessitating a periodical scraping of the interior of the pipe-lines. Much of the deposit which accumulates in the storage-tanks of crude oil is of the same material.

More important, however, is the occurrence of solid native paraffine, under the name of "ozokerite," or earth-wax. The best-known locality for this native paraffine is Boryslaw, in Eastern Galicia, although it is found also in the Caucasian oil district, and in Persia under the name of "neft-gil," and a few years ago was found in Southern Utah, in the United States. In color it varies from dark green to black, and possesses a lamellar or conchoidal fracture, according to the variety. It fuses between 56° and 74° C., or even higher. In chemical composition it does not differ much from the separated paraffine of petroleum oils.

4. BITUMEN AND ASPHALT.—We may have liquid bitumens, usually called *malthas*, and solid bitumens, called *asphalts*. Both may be considered as alteration products of petroleum hydrocarbons resulting from evaporation and oxidation.

Maltha (or mineral tar) was first found at Bechelbronn, in Alsace, and was studied by Boussingault, who described it as a viscid, tarry liquid of bituminous odor and a specific gravity of .966. It contains besides hydrocarbons both sulphur and nitrogen.

In the United States malthas are found in California in Kern, Ventura, and Santa Barbara Counties, as well as in Utah, Kentucky, Tennessee, and Texas. Those from California, which have been chemically examined, invariably contain some nitrogen present in the form of basic hydrocarbons. They also contain some water and dissolved gases.

The purest of the solid bitumens are known sometimes as "glance pitch" or "gum asphaltum." Prominent among them is gilsonite, which is found in the Uintah Indian reservation in Wasatch and Uintah Counties, Utah. The purity of this product (some ninety to ninety-eight per cent. soluble in carbon disulphide) is such that it finds large application in the manufacture of varnishes and insulating compounds, the production being some three thousand tons annually.

Of solid asphalts, those of greatest commercial importance are the Trinidad Lake asphalt from the Island of Trinidad in the West Indies and the Bermudez asphalt from Venezuela, South America. The first of these contains in the crude state 39.83 per cent. of bitumen, 33.99 per cent. of earthy matter, 9.31 per cent. of vegetable non-bituminous matter, and 16.87 per cent. of water. After refining the water is eliminated and the bitumen is raised to about sixty per cent. The Bermudez asphalt contains but 2.63 per cent. of mineral matter and over ninety per cent. of bitumen. The solid asphalts of California contain from sixty to ninety per cent. of bitumen, while the mineral matter in most cases is a very pure silica, or in some cases infusorial earth. Other solid asphalts, but less valuable, are those of Cuba and Syria, containing some seventy-five per cent. of a hard, brittle bitumen.

Very important also are the bituminous limestones or "rock asphalts" of Europe. Among these may be mentioned those of Seyssel, France, Val de Travers in the canton of Neufchâtel, Switzerland, Ragusa in Sicily, and Limmer and Vorwohle in Germany. These contain from five and three-tenths to fourteen per cent. of bitumen, and about eighty-six to ninety per cent. of carbonate of lime, and as they are largely used both in this country and in Europe in the manufacture of asphaltic mixtures or mastics, a table showing their exact composition is given:

| | Seyssel, France. | Val de Travers, Switzerland. | Ragusa, Sicily. | Limmer, Germany. | Vorwohle, Germany. |
|---|---|---|---|---|---|
| Bitumen | 8.15 | 10.15 | 8.92 | 14.30 | 5.37 |
| Calcium carbonate | 91.30 | 88.40 | 88.21 | 67.00 | 90.80 |
| Magnesium carbonate | .10 | .30 | .96 | . . . | .35 |
| Clay and oxide of iron | .15 | .25 | .91 | 17.52 | .59 |
| Sand | . . . | . . . | .60 | . . . | 2.55 |
| Insoluble | .10 | .45 | . . . | . . . | . . . |
| Loss | .20 | .45 | .40 | 1.18 | .34 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

In the United States the most important occurrence of bituminous limestone is that of Uvalde County, Texas, from which is obtained the product known as "litho-carbon," used in varnish-making and for insulating purposes.

Related to the natural asphalts are also such minerals as Albertite, from the Albert mines in New Brunswick, and the Ritchie mineral from Ritchie County, West Virginia.

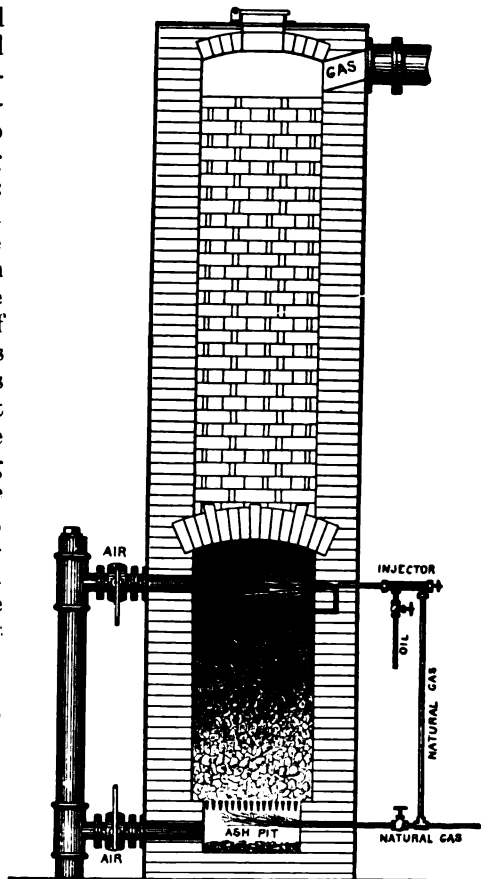
The Torbane mineral, from Bathgate, Scotland, and Boghead coal, together with bituminous shales, also should be noted here. They form the crude material for the Scotch paraffine distillation.

## II. Processes of Treatment.

1. Of Natural Gas.—If we refer to the composition of natural gas, as already stated, it will be seen that it is largely made up of methane and its homologues, with some nitrogen as impurity. The olefines, or "illuminating hydrocarbons" of ordinary coal-gas, are practically absent in most

cases. This at once indicates quite clearly the value of natural gas as a fuel and its lack of value in the natural state for illuminating purposes. But that it can be readily converted into an excellent illuminating gas has been shown, and in Western Pennsylvania, where natural gas is abundant, it is being used for illumination as well as for fuel. To illustrate the treatment that is necessary for the purpose we may describe the McKay and Critchlow process, which has proven quite successful in practice. The apparatus, as shown in Fig. 1, consists essentially like the water-gas generators of a combustion-chamber filled with coal brought to a white heat by an air-blast and a fixing-chamber above filled with fire-brick, where the gaseous products of the first reaction combine with oil vapors to form a permanent illuminating gas. The procedure is as follows: The fuel having been rendered thoroughly incandescent, and the fire-brick structure having been heated to a light orange tint, the air-blast is shut off, the lid of the cupola closed, and the gas outlet opened. Natural gas is then introduced into the ash-pit and forced up and through the incandescent fuel-bed, depositing its carbon on the surfaces of the fuel as decomposition is effected, and hydrogen gas is thus liberated, which, passing up through the open chamber, meets the vapors of the hydrocarbon, which is projected into the chambers by means of a steam- or gas-injector. All of these products of decomposition passing together into the upper or fixing chamber, a part of the hydrogen unites with the heavy hydrocarbons, producing the lighter hydrocarbons, while an intimate mixture of all the gases is effected, forming a completely permanent illuminating gas, which passes off through the water-seal, condensers, scrubbers, and purifiers to the holder in the ordinary way. Natural gas is used quite largely now with Welsbach burners, and an excellent illumination is thus obtained.

Fig. 1.

Natural gas is also burned for the production of a very pure grade of lamp-black. This manufacture, first carried out at Gambier, Ohio, is now introduced at various places in the oil regions of Pennsylvania. The gas is burned from rows of burners placed in such position that the flame impinges upon slate or metallic slabs or revolving cylinders, and there deposits

its carbon. In one building at Gambier, eighteen hundred burners have been used, consuming two hundred and seventy-five thousand cubic feet of gas per twenty-four hours.

2. OF CRUDE PETROLEUM.—As petroleum has been shown to be a mixture of hydrocarbons of different volatility, the first operation would naturally be to effect a partial separation of these hydrocarbons by a process of fractional distillation. But, in fact, simpler lines of treatment were first tried. It was found that crude oils spread out over warm water in tanks and exposed to the sun were much improved in gravity and consistency. This process was chiefly employed for the production of lubricating oils, and the products were called "sunned oils." This was followed by the application of methods of partial evaporation or concentration in stills, either by direct application of heat or by the use of steam coils, carefully avoiding overheating. The products are called "reduced oils," and form the best material for the manufacture of high-grade lubricating oils. They will be referred to again. The process to which the great bulk of crude petroleum is submitted, however, is that of fractional distillation continued to the eventual coking of the residue. As the most valuable of the several distillates is that which is to be used as illuminating oil, the percentage of that distillate obtainable is an important item in an oil refinery. A normally-conducted fractional distillation of Pennsylvania petroleum will give from thirty-five to fifty-five per cent. of oil suitable for illuminating purposes, and from twenty to thirty per cent. of lubricating oils. About 1865, however, it was found that if during the distillation the heavy vapors were made to drop back upon the hot oil in the still they became superheated and were decomposed. This process of destructive dis-

*The Results of a Normal Distillation of One Hundred Cubic Centimetres of Crude Oils are thus given by Engler:*

| CRUDE OIL FROM | Sp. gr. at 17° C. | Began to boil. | Came over under 150° C. | Between 150° C. and 300° C. | Over 300° C. |
|---|---|---|---|---|---|
| Pennsylvania (I.) . | 0.8175 | 82° C. | 21 per cent. | 38.25 per cent. | 40.75 per cent. |
| Pennsylvania (II.) . | 0.8010 | 74° C. | 31.5 per cent. | 35 per cent. | 33.5 per cent. |
| Galicia (Sloboda) . . | 0.8235 | 90° C. | 26.5 per cent. | 47 per cent. | 26.5 per cent |
| Baku (Bibieybat) . . | 0.8590 | 91° C. | 23 per cent. | 38 per cent. | 39 per cent. |
| Baku (Balakhani) . | 0.8710 | 105° C. | 8.5 per cent. | 39.5 per cent. | 52 per cent. |
| Alsace (Pechelbronn) | 0.9075 | 135° C. | 3 per cent. | 50 per cent. | 47 per cent. |
| Hanover (Oelheim) | 0.8990 | 170° C. | . . . . . . | 32 per cent. | 68 per cent. |

*The Commercial Results usually obtained, on the other hand, are thus stated by the same Authority (Wagner's Jahresbericht, 1886, p. 1077).*

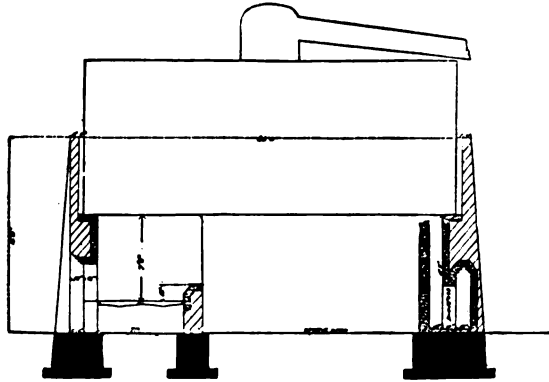
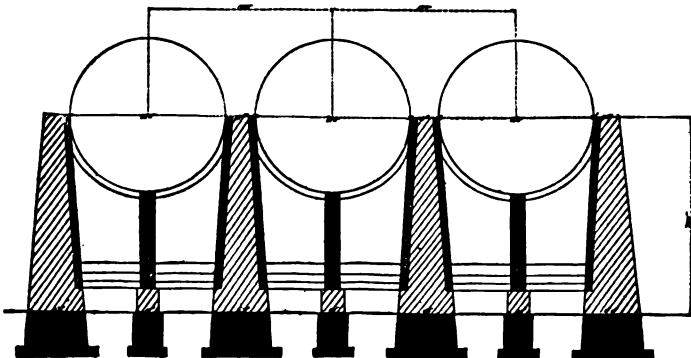
| CRUDE OIL FROM | Benzine and volatile oils. | Burning oil, first quality. | Burning oil, second quality. | Residuum. |
|---|---|---|---|---|
| Pennsylvania . . . . . . . . . | 10 to 20 | 60 to 75 | | 5 to 10 |
| Galicia . . . . . . . . . . . . | 3 to 6 | 55 to 65 | | 30 to 40 |
| Alsace . . . . . . . . . . . | . . . | 35 to 45 | | 55 to 60 |
| Roumania . . . . . . . . . . | 4 | 60 to 70 | | 25 to 35 |
| Baku (Bibieybat) . . . . . . . | 10.5 | 40 | 13 5 | 36 |
| Baku (Balakhani) . . . . . . . | 5 to 6 | 27 to 33 | 5 to 6 | 50 to 60 |

tillation or "cracking" allowed of a notable increase of the illuminating oil fraction at the expense of the lubricating oil. So at present some

seventy-five to eighty per cent. of burning oil is obtained, while the residuum from which the lubricating oil is gotten is reduced to six per cent.

A general outline of the petroleum refining process as at present conducted is presented in tabular form on the accompanying diagram.

The process is generally divided into two quite distinct parts. The benzine and burning oil distillate are run from the same still, when the fluid residuum is transferred to what are usually called "tar-stills," in which the rest of the distilling operation is conducted.

FIG. 2.

Lateral vertical section of cylindrical still.

Transverse vertical section of cylindrical still.

The crude-oil stills are of two forms, the cylindrical still, as illustrated in section in Fig. 2, and the "cheese-box" still, although the latter is little used now. The former consists of a cylinder of boiler-plate, the lower half being generally of steel, thirty feet in length by twelve feet six inches in diameter. This still is set horizontally, as shown in the sectional view, in a furnace of brick-work, usually so constructed that the upper part of the still is exposed to the air. The "cheese-box" still has a body and dome-shaped top of boiler-plate and a double-curved bottom of steel plate. It is thirty feet in diameter and nine feet in height, and is set on a series of brick arches. The working charge of the cylindrical stills is

CRUDE PETROLEUM.
DISTILLED.
BENZINE DISTILLATE
Cut off at 70° B. to 62° B.
Redistilled by the aid of special condensing apparatus.
I. Cymogene, boiling-point, 32° F., and Rhigolene, boiling-point, 65° F.
II. Petroleum ether, 88° B., and Gasolene, 71° B.
III. Naphtha, 70° B., and Benzine, 62° B.
BURNING OIL DISTILLATE.
Low-test burning oil cut off at 56° B.
High-test burning oil run by aid of "cracking" until 6 per cent. is left.
All burning-oil fractions are submitted to the following treatment:
Treated with 1½ per cent. of sulphuric acid, sludge acid run off, washed with water, and washings run off. Treated with 1 per cent. caustic soda solution of 12° B., and washed.
110° fire-test oil.
150° fire-test oil.
RESIDUUM.
If the distillation has been carried on by the "vacuum process," the residuum is known as a "reduced oil," and is used in its entirety for the manufacture of filtered lubricating oils and vaseline.
Otherwise the residuum is redistilled from residuum or tar stills.
First runnings returned to burning-oil fraction.
Paraffine oil.
Treated with 3 to 5 per cent. of sulphuric acid in paraffine agitator, washed with water and sal soda.
Chilled by artificial means.
CRUDE SCALE PARAFFINE or "soft wax."
Broken up, melted, recrystallized, and washed with benzine.
PURIFIED SCALE or "white wax."
This, remelted and filtered through bone-black or clay, yields
Block paraffine
Lubricating oil.
Yellow wax.
Coke.

about seven hundred barrels of crude oil, although occasionally stills of one thousand barrels' capacity have been used. The still is usually provided with coils of steam-pipes, both closed and perforated. The steam, issuing in jets from the perforated pipe, has been found to facilitate distillation by carrying over mechanically the oil vapors.

The condensing apparatus varies somewhat in the details of its construction, but consists essentially of long coils of pipe immersed in tanks, through which water is kept flowing. The terminal portions of the condensing pipes all converge and enter the receiving house within a few inches of each other. Near the extremity of each a trap in the pipe is made for the purpose of carrying away the uncondensable vapor. This may be allowed to escape, or is burned underneath the boilers or stills, effecting thereby a large saving in fuel. The condensing pipes generally deliver into box-like receptacles, with plate-glass sides, through which the running of the distillate can be observed, and from which test portions can be taken from time to time for the proper control of the process.

The tar-stills are usually of steel, cylindrical in shape, holding about two hundred and sixty barrels, and are set in groups of two or more, surrounded by brick-work. They are either upright or horizontally placed, usage inclining now to the latter position. Vacuum-stills have been and are still used to some extent, especially in the preparation of reduced oils for the manufacture of lubricants and products like vaseline. Of course, the evaporation in these stills takes place rapidly, and at the lowest temperature possible, insuring a fractional distillation and not a decomposition. If superheated steam be used, moreover, instead of direct firing, it is possible to reduce oils to 26° B. without any production of pyrogenic products. A still arranged with superheated steam is shown in Fig. 3. Continuous distillation has not proved commercially successful in the United States. In Russia, on the other hand, continuous distillation has been eminently successful, being especially suited to Baku petroleum, as the quantity of burning oil separated being comparatively small, the residuum is not very much less fluid than the crude oil. The stills, each of the capacity of four thousand four hundred gallons, are arranged in groups or series of not more than twenty-five, as shown in Figs. 4 and 5, one of which is a front view, and the other a section, and a stream of oil is kept continuously flowing through the entire number. The crude oil, entering the first still, parts with its most volatile constituents;

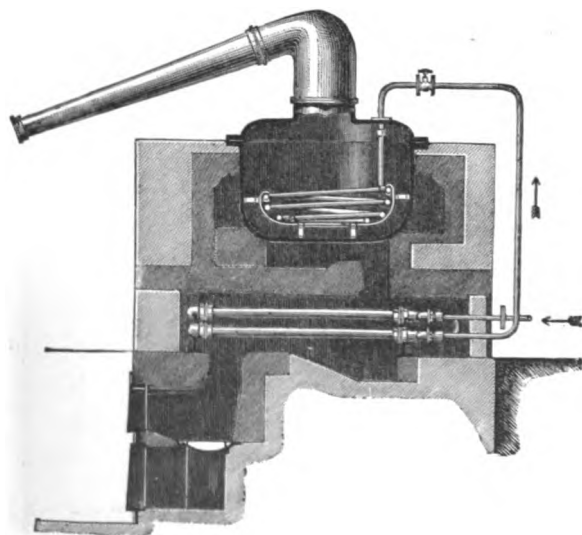
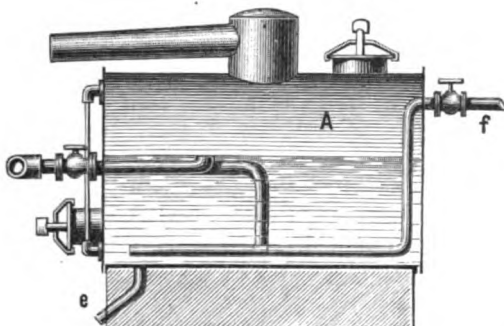
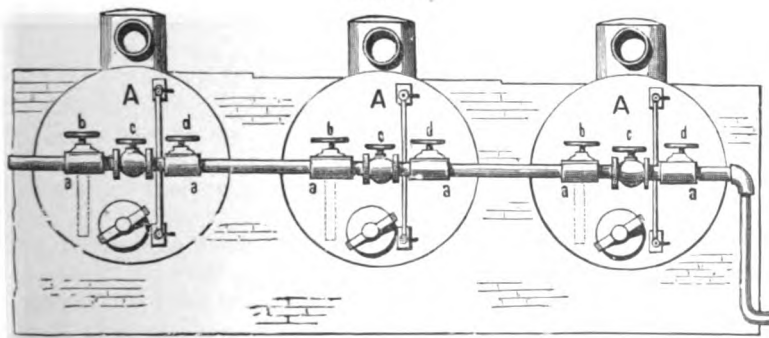



FIG. 3.

passing into the next still, has rather less volatile hydrocarbons distilled from it; and, finally, flows from the last still in the condition of residuum, which in Russia is termed *astatki*, or *masut*. The several stills are maintained at temperatures corresponding with the boiling-points of the products to be volatilized. Superheated steam is used for all the stills, the steam being delivered partly under the oil and partly above the level of the oil,—that is, in the vapor space above. The fuel used under all the stills in Baku is petroleum residuum, or *astatki*.

Fig. 4.

To recur, now, to the products of the first rough distillation of crude oil, the first fraction, known as the "benzine distillate," and amounting usually to twelve per cent. of the crude oil, is redistilled by steam heat in cylindrical stills, holding five hundred barrels, and is sometimes separated into the following products: cymogene, 100° to 110° B. gravity; rhigolene, 90° to 100° B. gravity; gasolene, 80° to 90° B. gravity; naphtha, 70° to 76° B. gravity; benzine, 62° to 70° B. gravity.

The time occupied in working the charge is about forty-eight hours. The percentage of these products varies, but, as a rule, amounts to about twenty-five per cent. of the first three collectively, rather more than twenty-five per cent. of the naphtha, and about forty per cent. of the benzine. The deodorization of the benzine which is to be used for solvent purposes in pharmacy or the arts is effected somewhat after the manner to be described under burning oils by the action of sulphuric acid. Only the proportion of acid used is much smaller and the agitation is effected by revolving paddles instead of by an air-blast. One-half of one per cent. is sufficient

Fig. 5.

in this case. Other processes have been proposed for the deodorization, such as the use of mixtures of sulphuric and nitric acids with alcohol, which produce ethereal products which are said to neutralize and destroy the benzine odor.

The treatment of the illuminating oil fraction is a more important

process. It must be freed from the empyreumatic products resulting from the distillation, which give it both color and disagreeable odor. To effect this it is subjected to a treatment with sulphuric acid, washing with water and a solution of caustic soda. This operation is conducted in tall cylindrical tanks of wrought iron, lined with sheet-lead, which are called "agitators." The bottom is funnel-shaped, terminating in a pipe furnished with a stopcock for drawing off the refuse acid and soda washings. The distillate to be treated must be cooled to at least 60° F., and before the main body of acid is added for the treatment, any water present must be carefully withdrawn. This is done by starting the agitation of the oil by the air-pump and introducing a small quantity of acid. This is allowed to settle, and withdrawn. The oil is now agitated, and about one-half of the charge of acid is introduced gradually from above. The agitation is now to be continued as long as action is indicated by rise of temperature, when the dark "sludge acid" is allowed to settle, and withdrawn. The remaining portion of acid is added, and a second thorough agitation takes place. The whole charge of acid needed for an average distillate is about one and one-half to two per cent., or about six pounds of acid to the barrel of oil. The acid, as drawn off, is dark-blue or reddish-brown in color, and is charged with the sulpho-compounds of the olefines, while free sulphur dioxide gas is present in abundance. The oil, after treatment, consists of the paraffin hydrocarbons almost freed from admixture with olefines. In color it has been changed from brownish-yellow to a very light straw shade. The oil is now washed with water introduced through a perforated pipe running around the upper circumference of the tank. This water percolates through the body of the oil, removes the acid, and is allowed to escape in a constant stream from the bottom. When the wash-water shows no appreciable acid taste or reaction, the washing is stopped, and about one per cent. of a caustic soda solution of 12° B. is introduced, and the oil is again agitated. When this is drawn off, the oil is ready for the settling tanks. A washing with water after the soda treatment is sometimes followed, but it is not general. A washing with dilute ammonia is also sometimes used to remove the dissolved sulpho-compounds. The settling tanks are shallow tanks, exposed to air and light on the sides, and here any water contained in the oil settles out, and the oil becomes clear and brilliant. They are provided with steam-coils for gently warming the oil in cold weather to facilitate this separation. A spraying of the finished oil to raise the fire-test by volatilizing a small quantity of the lighter hydrocarbon present was formerly practised at this stage, but exacter control of the distillation has rendered it no longer necessary.

The Lima oil and Canadian oil, which, as before stated, contain sulphur impurity, cannot be refined and good illuminating oils obtained by this simple treatment with acid and alkali. Various methods of treatment have been proposed and patented for these oils, such as the alternate treatment with litharge and caustic soda, distillation over finely-divided copper and iron, but the method finally adopted and now in successful use is to distil over a mixture of oxides of copper and lead, which take up the sulphur. The oil is also sold for fuel purposes. This latter utilization has been one of great importance, and it is employed in all classes of manufacturing establishments with great success and economy as a substitute for solid fuel. With the aid of injector burners, it has been found possible to use it in smelting and annealing furnaces, in all kinds of forges, in burning brick,

tiles, and lime, and for raising steam with all forms of boilers. It is used in these burners in connection with either steam or compressed air.

The residuum of the original crude-oil distillation is, as was said, distilled from the "tar-stills." The first runnings, constituting from twenty to twenty-five per cent., will have a gravity of 38° B., and are returned to the crude-oil tank for redistillation, or are treated and purified as burning oil. The paraffine oil which now runs over may be caught in separate lots as it deepens in color and increases in density, or it may be all received together to be treated in the paraffine agitator with acid and purified for the separation of paraffine wax. The agitator in this case must be provided with steam-pipes, so that its contents can be kept perfectly liquid, and the charge of acid is larger, amounting to three, four, or even five per cent. The treatment includes the usual washing with water and soda all at the proper temperature.* The "sludge" becomes quite solid on standing, and is not worked over. After settling, the paraffine oil goes to the chill-rooms, where, by the aid of the ammonia refrigerating machines and the circulation of cooled brine, the whole mass is brought to a semi-solid condition. This is pressed between bagging by hydraulic pressure, or is filter-pressed, and the refined heavy oil which drains off is collected as lubricating oil. Its gravity should be about 32° B., fire-test, 325° F., and cold test, 30° F. The press-cake may be broken up, melted, and recrystallized, and then submitted to still greater pressure at a higher temperature (70° F.) than before, when it is gotten as "refined wax." To convert it into block paraffine, it must be washed with benzine, pressed, melted, and filtered through bone-black or other filtering medium, when it is gotten perfectly colorless and solidifying to a hard, translucent block. The characters of paraffine will be referred to farther on.

The distillation of residuum is continued until the bottom of the still becomes red-hot, when yellow vapors issue from the tail-pipe, and a dense resinous product, of a light-yellow color, and nearly solid consistency, distils over. This "yellow wax" contains anthracene, chrysene, picene, and other higher pyrogenic hydrocarbons. Its only use at present is to add it to paraffine oils to increase density and lower cold test. Its chemical character will be referred to again.

The coke remaining in the tar-still at the end of the process amounts to about twelve per cent., and is largely used in the manufacture of electric-light carbons. Reduced oils gotten by careful driving off of the light fractions of the crude petroleum, without cracking, as stated before, are of great value as lubricants. They are generally made by vacuum distillation and the use of superheated steam instead of direct firing. They are either brought into the market at once, without further treatment, or after a bone-black or clay filtration. This production of filtered oils is usually combined with the manufacture of vaseline, or *petrolatum*, as it is now known in the "United States Pharmacopœia." Taking a vacuum residuum as the raw material, this is melted and run on to filters of fine granular well-dried bone-black. The filters are either steam-jacketed or are placed in rooms heated by steam-coils to 120° F. or higher. The first runnings are colorless, and all up to a certain grade of color go to the manufacture

* With the lubricating oils from certain crude petroleums, it is found advantageous *not* to wash after the acid treatment, but to treat immediately with a strong caustic lye (of 33° B.), and then to wash as a final step. This is said to prevent the emulsifying of the oil and water which sometimes takes place and greatly retards the separating out of the oil.

of vaseline. Beyond that the filtrate is known as "filtered cylinder oil," and is used as a lubricant exclusively.

3. OF OZOKERITE AND NATURAL PARAFFINE.—The Galician ozokerite is in the main a natural paraffine, but contains some oil in mechanical admixture. Until within ten to twelve years ago it was worked exclusively for the production of paraffine, but now not more than one-third of the annual production is so worked. The most of it is distilled, yielding five per cent. of benzine, fifteen to twenty per cent. of illuminating oil, fifteen per cent. of "blue oil," and about fifty per cent. of paraffine. The "blue oil" is a buttery-like mixture of heavy oils with paraffine crystals, and corresponds to a paraffine oil as distilled from petroleum. It is run into filter-presses and pressed, first cold, and then the press-cake broken up and pressed warm to remove the adhering oils. If the paraffine scale so obtained is to be worked up into block paraffine, it is repeatedly treated with benzine of not over .785 specific gravity, and pressed, then melted and filtered through bone-black, as before described under petroleum paraffine.

If the ozokerite is to be worked up as a whole into the wax-like product known as *Ceresine*, the operation may be conducted in one of two ways. The older method was, after a preliminary melting of the ozokerite, to free it from earthy impurities, and continuing the heating until all water was driven out of the melted mass to treat it with ten per cent. of sulphuric acid as long as sulphurous oxide was evolved. This was followed by treatment with water and soda solution. To more thoroughly separate out the black carbonaceous matter produced by the action of the sulphuric acid, one-half to one per cent. of stearic acid is added, and this then saponified with caustic soda. The soap so formed carries down all carbonaceous matter with it, and allows the ceresine to be filtered clear by using filter-paper. The product is the *Yellow Ceresine*, much resembling beeswax. The *White Ceresine*, resembling bleached beeswax, is gotten by melting the yellow ceresine by the aid of steam, digesting it with bone-black, with frequent stirring, and filtering through paper. The newer method, more frequently followed now, is to extract the ozokerite with benzine and ligroine. The forms of apparatus devised for this purpose allow of a complete exhaustion of the ozokerite mass and a subsequent recovery of the solvent used in the extraction.

The natural paraffine that separates spontaneously from crude petroleum, and accumulates at times, as before mentioned, in pipe-lines, etc., is chiefly used as a basis for the manufacture of vaseline and similar products, being melted and filtered through bone-black, as already described.

4. OF NATURAL BITUMENS AND ASPHALTS AND OF BITUMINOUS SHALES.—The asphalt or solid bitumen from the Island of Trinidad is exported largely to the United States, where it is used in the manufacture of roofing materials and of asphalt pavements. It yields from one and three-fourths to two and a half per cent. of paraffine on distillation, and contains sulphur as an invariable constituent. Efforts made to manufacture illuminating and other oils from the asphalt have failed of practical results.

Within recent years artificial asphalts have been made by a variety of methods. As already mentioned, the California petroleums all seem to have an asphaltic instead of a paraffine base. Hence the residuum from the refining of California crude oils is manufactured into artificial asphalts. As much as eleven per cent. of artificial asphalt has been obtained in practice from Ventura County petroleum.

Again, artificial asphalts have been made by treating Lima, Ohio, petroleum with a current of heated air until all volatile products are driven out. The product *byerlite* is thus obtained.

Still another process consists of melting oil residuums with sulphur and heating until a product is obtained which becomes solid on cooling, while hydrogen sulphide is set free. By far the most interesting production of artificial asphalt is that of Dr. W. C. Day, who distilled a mixture of fish and pine wood and then submitted the oil obtained to a second destructive distillation. The residuum left when the distillation was carried to about 425° C. solidified to a black, shining mass, which in physical properties and chemical composition strikingly resembles Utah gilsonite.

Very much more important are the industries based upon the distillation of bituminous shales. As these shales do not contain either liquid or solid hydrocarbons as such, but much more complex compounds called bitumens, the distillation is exclusively a destructive one, and the character of the distillation products becomes dependent upon the conditions of the operation, temperature being the most important consideration. The theory of destructive distillation will be entered upon at length later (see p. 347), and we will here only say that for paraffine and illuminating oil production the distillation is essentially a low-temperature one.

The material originally used in Scotland was Boghead coal, or the Torbane Hill mineral from Bathgate, near Glasgow, which was exhausted in 1872. This yielded thirty-three per cent. of tar or oily distillate and one to one and one-half per cent. of crude paraffine. At present shales are used, which furnish about thirteen per cent. of tar. The material for the German paraffine production is an earthy brown coal, which, when dry, is of a light-brownish or yellowish color and crumbling character ; it yields on an average 8.1 per cent. of tar and .6 per cent. of paraffine. The shales are usually distilled with some steam, which increases the amount of the tar, as well as the ammonia from the shale. The distillation may be intermittent, but in Scotland is now carried on in a continuous process by the two methods devised by Henderson and by Young & Beilby respectively, the exhausted shale being dropped from the bottom of the upright retort into a combustion-chamber beneath. As the spent shale sometimes contains as much as from twelve to fourteen per cent. of carbon, this, with the uncondensed gas of the distillation, suffices for fuel. The several products of the distillation are (1) gas, which is freed from gasolene vapors by passing through a coke tower, down which heavy oil is trickling ; (2) watery or ammoniacal liquor, which is obtained to the amount of from sixty-five to eighty gallons per ton of shale, and yields from fourteen to eighteen pounds of sulphate of ammonia per ton worked ; (3) oily liquor, or tar proper, of dark greenish color, and ranging from .865 to .880 in specific gravity, varying in amount from thirty to thirty-three gallons per ton of shale used. This is distilled in cast-iron stills holding from two hundred to two thousand gallons, for the purpose of purifying it, until only coke amounting to from five to ten per cent. of the tar is left. The mixed distillates (the paraffine magma being added to the others), according to the usage of the German paraffine-works, are stirred with two per cent. by volume of caustic soda solution in order to take up phenols and "creosote," together with other acid products ; the soda washings drawn off below, and the supernatant liquid, after washing with water, is agitated with five per cent. of sulphuric acid. The refined oil is now fractionally distilled. The first fraction (specific gravity .60 to

.68) is a gasolene used for carburetting illuminating gas; the second (specific gravity .68 to .76) is naphtha, used as a solvent; the third (specific gravity .81 to .82) is illuminating oil; the fourth lubricating oil (specific gravity .865 to .900). The next distillate solidifies on cooling, yielding brown crystals of hard paraffine, whose mother-liquor, removed by a filter-press, is "blue oil," whence more but soft crystals can be obtained by artificial refrigeration. The mother-liquid of these is again treated with vitriol and soda and distilled; the earlier fractions constitute heavy illuminating oil, the later lubricating oil. The percentage of solid paraffine gotten from the crude shale oil is from eleven to twelve and a half per cent. The shale oil does not yield any product corresponding to vaseline. B. Hübner, a German paraffine manufacturer, believing that the distillations of the process just described act injuriously upon the quantity and hardness of the paraffine obtained, has modified the process as follows. He treats the crude shale oil with sulphuric acid, and, after the separation of this, distils the oil over several per cent. of slaked lime. After the crystallization of the paraffine from the distillate, it is purified by washing with shale oils and pressing. He thus avoids one distillation and obtains a larger yield of paraffine, distinctly harder in character than the usual product.

In the Scotch shale-works the distilled oil is treated first with sulphuric acid and then with caustic soda, as in the purifying of petroleum oils, and then fractionally distilled. These fractions are again treated with acid and alkali before being considered pure enough for the market. In some works (as those at Broxburn) continuous distillation is practised, so that a set of three boiler stills and two residue- or coking-stills, used together, can put through thirty-five thousand gallons of crude oil per day. The solid paraffine, by careful processes of extraction, can be brought up to twelve and a half per cent.

## III. Products.

1. From Natural Gas.—(*a*) *Fuel Gas.*—The great value of natural gas as fuel for manufacturing and industrial purposes has only been realized in recent years, and it was rapidly introduced as a substitute for coal and coke. In Western Pennsylvania and Ohio, particularly in Pittsburg and its vicinity, for manufacturing purposes, it had for a time almost entirely displaced coal and coke, but its production has reached a maximum, and is now rapidly falling off despite the opening of new wells That natural gas, largely made up of methane and similar hydrocarbons, is one of the best of gaseous fuels is seen from the accompanying table, prepared by a committee of the American Society of Mechanical Engineers:

*Table showing Comparative Effects of Different Gas Fuels.*

| | Heat units yielded by one cubic foot. | Number of cubic feet needed to evaporate 100 pounds of water at 212° F. |
|---|---|---|
| Hydrogen | 183.1 | 293 |
| Water gas (from coke) | 153.1 | 351 |
| Blast-furnace gas | 51.8 | 1038 |
| Carbonic oxide | 178.3 | 313 |
| Marsh gas | 571.0 | 93.8 |

The comparison of its work with that accomplished with solid fuel, as carried out at the works of Carnegie, Bros. & Co., in Pittsburg, is also given by the same committee. Using the best-selected coal, and charging the furnace in such manner as to obtain the best results, the maximum

with coal was nine pounds of water evaporated to the pound of coal consumed. "In making the calculations, the standard seventy-six-pound bushel of the Pittsburg district was used; six hundred and eighty-four pounds of water were evaporated per bushel, which was 60.90 per cent. of the theoretical value of the coal. When gas was burned under the same boiler, but with a different furnace, and taking a pound of gas to be equal to 23.5 cubic feet, the amount of water evaporated was found to be 20.31 pounds, or 83.40 per cent. of the theoretical heat-units were utilized."

(*b*) *Illuminating Gas.*—The processes for converting natural gas into illuminating gas have already been referred to, and the McKay & Critchlow process described in detail. The production by this process of a permanent gas, showing no condensation of vapors at the drips, and of eighteen to twenty candle-power, is said to have been demonstrated at Beaver Falls, Pa., and elsewhere.

(*c*) *Lamp-black.*—The burning of natural gas so as to cause separation of carbon, which is then collected as lamp-black, has been referred to. The lamp-black so manufactured has been shown to be of great purity. It is miscible with water, does not color ether, and is free from oily matter. A sample of it analyzed by Professor J. W. Mallet, of the University of Virginia, gave the following results: Specific gravity at 17° C., after complete exhaustion of air, 1.729. The percentage of composition was as follows:

| | |
|---|---|
| Carbon | 95.057 |
| Hydrogen | 0.665 |
| Nitrogen | 0.776 |
| Carbon monoxide | 1.378 |
| Carbon dioxide | 1.386 |
| Water | 0.622 |
| Ash ($Fe_2O_3$ and CuO) | 0.056 |
| | 99.940 |

(*d*) *Electric-light Carbons.*—Still another use for carbon from natural gas is the manufacture of carbons for electric arc-lights, the purity of the material making a very pure and uniform carbon pencil possible.

2. From Petroleum.—The names of commercial products obtained from petroleum have, of course, been almost infinitely varied, as each manufacturer has his trade names for his special products. We shall only designate the generally-accepted classes of products. Beginning with the lightest, we have:

*Cymogene*, gaseous at ordinary temperatures, but liquefiable by cold or pressure. Boiling-point, 0° C. (32° F.). Specific gravity, 110° B. Used in the manufacture of artificial ice.

*Rhigolene*, condensable by the use of ice and salt. Boiling-point, 18.3° C. (65° F.). Specific gravity, 0.60 or 100° B. Used as an anæsthetic for medical purposes.

*Petroleum Ether* (Sherwood oil).—Boiling-point, 40° to 70° C. Specific gravity, .650 to .660, or 85° to 80° B. Used as a solvent for caoutchouc and fatty oils, and for carburetting air in gas-machines.

*Gasolene* (canadol).—Boiling-point, 70° to 90° C. Specific gravity, .660 to .690, or 80° to 75° B. Used in the extraction of oil from oil-seeds and in carburetting coal-gas.

*Naphtha* (Danforth's oil).—Boiling-point, 80° to 110° C. Specific gravity, .690 to .700, or 76° to 70° B. Used for burning in vapor-stoves and street-lamps, as a solvent for resins in making varnishes and in the manufacture of oil-cloths.

*Ligroine.*—Boiling-point, 80° to 120° C. Specific gravity, .710 to .730, or 67° to 62° B. For solvent purposes in pharmacy and for burning in sponge-lamps.

*Benzine* (deodorized).—Boiling-point, 120° to 150° C. Specific gravity, .730 to .750, or 62° to 57° B. Used as a substitute for turpentine, for cleaning printers' type, and for dyers', scourers', and painters' use.

*Burning Oil, or Kerosene.*—The different burning oils are known often by special names, of which the number is legion, but they are graded by the American petroleum exporters chiefly according to the two standards of color and fire-test. The colors range from pale-yellow (standard white) to straw (prime-white) and colorless (water-white). The fire-tests (see p. 33), to which the commercial oils are mostly brought, are 110° F., 120° F., and 150° F.; that of 110° going mainly to the continent of Europe and to China and Japan, and that of 120° to England. An oil of 150° F., fire-test, and water-white in color, is known in the trade as "headlight oil." An oil of 300° F., fire-test, and specific gravity .829, is known as "mineral sperm," or "mineral colza oil." "Pyronaphtha" is a product from Russian petroleum, somewhat similar to mineral sperm oil. It has a specific gravity of .865, and fire-test of 265° F.

*Lubricating oils* from petroleum have assumed an importance which is increasing every year. Some crude petroleums, like those of Franklin and Smith's Ferry, Pa.; Mecca, Ohio; Volcano, W. Va., and other localities, are natural lubricating oils, requiring little or no treatment to fit them for use. The other petroleum lubricating oils are gotten in one of two ways. Either by driving off the light hydrocarbons from the crude oil, yielding what is called a "reduced oil" (see p. 25), or they are the oils gotten by distilling the petroleum residuums in tar-stills.

The lightest of the lubricating oils, varying in gravity from 32° B. to 38° B., are frequently called "neutral oils." They are largely used for the purpose of mixing with animal or vegetable oils, and it is therefore necessary that they should be thoroughly deodorized, decolorized, and deprived of the blue fluorescence or "bloom" characteristic of petroleum distillates that contain paraffine. The first two results are accomplished by bone-black or clay filtration, the last in various ways, such as treatment with nitric acid, addition of small quantities of nitro-naphtha'enes, etc.

Heavier lubricating oils are called "spindle" and "cylinder" oils. The most important characters to be possessed by these oils is high fire-test, low cold-test, and a high viscosity. (See analytical tests, p. 34.)

In the matter of lubricating oils the Russian products are, it is now admitted, distinctly superior in most respects to the American. This is because of the entire difference in the chemical composition of the two, the hydrocarbons characteristic of the Russian oil being heavier and showing less tendency to solidify at low temperatures than those of the American oils. The following statement from Boverton Redwood will illustrate this:

| | Viscosity at 70° F. | Viscosity at 120° F. | Loss in viscosity, per cent. |
|---|---|---|---|
| Russian oil (sp. gr. .913) | 1400 | 166 | 88 |
| American oil (sp. gr. .914) | 231 | 66 | 71 |
| Russian oil (sp. gr. .907) | 649 | 135 | 79 |
| American oil (sp. gr. .907) | 171 | 58 | 66 |
| Russian oil (sp. gr. .898) | 173 | 56 | 67 |
| American oil (sp. gr. .891) | 81 | 40 | 50 |
| Refined rape oil (for comparison) | 321 | 112 | 65 |

It is true that the disproportion is chiefly at lower temperatures, the Russian oil losing its body relatively faster than the less viscous American oil.

*Paraffine* differs somewhat in its hardness and melting point according to the source from which it is derived. The petroleum paraffine is manufactured generally in three qualities, fusing at 125° F. (51.6° C.), 128° F. (53.3° C.), and 135° F. (57.3° C.), respectively, paraffine from shales melts at 56° C., while that from Rangoon tar melts at 61° C. and that from ozokerite at 62° C. The harder varieties are bluish-white, translucent, and glassy on the surface, while the softer varieties are alabaster-white, dull in lustre and only translucent when heated. The harder varieties are resonant. Paraffine is readily soluble in ether, benzene, and all light hydrocarbons, ethereal and fatty oils and carbon disulphide, not entirely in absolute alcohol; while ordinary alcohol only takes up 3.5 per cent. of it. It mixes with stearine, spermaceti, and wax in all proportions. Exposed for some time under a slight pressure to a temperature below its melting point, paraffine wax undergoes a molecular change and becomes transparent; but upon a change of temperature, or upon being struck, the original translucent appearance returns.

The harder variety of paraffine is used chiefly in candle-making, for which purpose, however, a small proportion (five per cent.) of stearic acid must be added to it to prevent the softening and bending of the candle. It is also used for finishing calicoes and woven goods, to the surface of which it imparts lustre. The softer varieties are used for mixing with wax and stearic acid in candle-making, for the preparation of translucent and waterproof paper of all grades, for impregnating Swedish matches, for the adulteration of "chewing-gums," and, in recent years, for "enfleurage" or extracting delicate perfumes from flowers.

3. From Ozokerite and Natural Paraffine.—The character of several of the products now obtained from Galician ozokerite, viz., illuminating and lubricating oils and paraffine, has been sufficiently described under other heads. The peculiar product known as *Ceresine*, gotten from ozokerite without distillation, remains to be described. It resembles beeswax very greatly in appearance, but is of lower specific gravity, ranging from .915 to .925, while wax is from .963 to .969. The fusing point of ceresine varies from 68° C. to 80° C. Ceresine, with a fusing point of over 75° C., shows a fracture and structure like that of wax. Its behavior to water, alcohol, ether, chloroform, fatty and ethereal oils is exactly like that of paraffine. Ceresine is extensively used as a substitute for wax as well as for most of the uses before given for paraffine. It is commended especially for the formation of matrices for galvano-plastic work, proving in this respect superior to gutta-percha. It is also being used instead of gutta-percha for hydrofluoric acid bottles.

4. From Bitumens, Asphalts, and Bituminous Shales.—It is only from the latter of these that products of commercial importance are derived. From the crude shale oil, already described, the following products are obtained:

*Shale Oil Benzine.*—Specific gravity .665 to .720, boiling-point 80° to 90° C., is colorless, of ethereal odor, and slightly peppermint-like taste. It is used somewhat as a cleansing benzine, but mainly in the purifying of the shale paraffine.

*Photogene* (shale naphtha).—Specific gravity .720 to .810, boiling-point 145° to 150° C., has a slight ethereal odor and peppery taste. It dissolves

sulphur, phosphorus, iodine, fats, resins, caoutchouc, etc. It is used somewhat for illuminating purposes and for dissolving the fat from bones and bleaching them in the preparation of artificial ivory.

*Solar oil* comes into the market, according to Grotowski, in two grades, known as *prima* and *secunda* oils, one with specific gravity .825 to .830 and a boiling-point 175° to 180° C., and the other with specific gravity .830 to .835 and a boiling-point 195° to 200° C. The oils are of slight, yellowish color, and on exposure to air and light lose their free burning qualities, somewhat through the resinifying of the trace of creosote which may remain in them. The fire-test of the solar oil is generally above 100° C., and they are in general both cheap and excellent burning oils.

*Paraffine Oil.*—The paraffine itself has been described under a previous heading. The expressed paraffine oil is used considerably as a lubricating oil, but is of greatest importance for gas-making. The gas from this paraffine oil is especially rich in illuminating hydrocarbons and is free from the ordinary impurities of coal-gas. It is extensively manufactured in Germany, in the Hirzel and Pintsch forms of apparatus, and in England by the Pintsch, Keith, and Alexander & Patterson processes, and compressed for use in railway carriages, etc. Its characters will be referred to more especially under the heading of illuminating gases.

5. VASELINE.—This product (*petrolatum* of the United States Pharmacopœia and *unguentum paraffini* of the German Pharmacopœia) may be obtained from several of the raw materials already mentioned. In the United States, as the name *petrolatum* indicates, it is a petroleum product and may be called "natural vaseline," as it is merely a purified preparation of naturally existing petroleum constituents; in Germany, and elsewhere in Europe, it is either extracted from other sources (pomade ozokerine), or, as the name *unguentum paraffini* indicates, it is an "artificial vaseline" made by the solution of paraffine in paraffine oil. American vaseline, as made by the Chesebrough Company and others, is gotten by taking a vacuum residuum (see p. 25) and, without any treatment with sulphuric acid or other chemicals, simply filtering it through heated bone-black. In this way the amorphous character of the hydrocarbons is not changed and no crystalline paraffine is produced, as would be the case if it were a distillation product, and, moreover, no traces of sulphonic acids can remain from the acid treatment to interfere with its use as a basis of medicinal ointments. The *petrolatum* of the United States Pharmacopœia may be either a soft variety, melting at 40° C. (104° F.), or a firmer variety, melting at 51° C. (125° F.).

The German vaseline, or *unguentum paraffini*, is made by taking one part of ceresine (*paraffinum solidum*) and dissolving it in three parts of a paraffine shale oil, known as "vaseline oil" (*paraffinum liquidum*). This artificial vaseline, as Engler and Böhm have shown,* easily becomes granular on chilling, and shows its composite nature moreover by readily separating on distillation into ceresine and oil. The natural vaseline has greater homogeneity and is more viscous, although at high temperatures it seems to absorb more oxygen then the artificial preparation. At temperatures not exceeding 30° C. the oxygen absorption seems to be practically nothing in either case.

Vaseline is largely used in pharmacy and medical practice as a basis of ointments and pomades.

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* Dingler, Polytech. Journal, 262, p. 468.

## IV. Analytical Tests and Methods.

1. For Natural Gas.—These are the methods employed for the analysis of all varieties of illuminating gas, and will be referred to under that heading. (See p. 387.)

2. For Crude Petroleum.—According to the rule of the New York Produce Exchange, "crude petroleum shall be understood to be pure natural oil, neither steamed nor treated, free from water, sediment, or any adulteration, of the gravity of 43° to 48° B." (0.809 to 0.786 sp. gr.). In order to determine whether the petroleum is a "pure natural oil" a sample is subjected to fractional distillation, each fraction being one-tenth of the crude oil by volume, and the density of the several distillates is determined. The regular gradation of the densities of the fractions so obtained is taken as a satisfactory indication that the oil is a natural product.

Fig. 6.

To judge of the commercial value of a crude petroleum a fractional distillation is also desirable. For this purpose Engler's system of distillation is to be recommended. He uses a distillation flask, the shape and dimensions of which in cubic centimetres are to be seen in Fig. 6. One hundred cubic centimetres of the oil is introduced into the flask by the aid of a pipette, and heat is applied. At first wire gauze is interposed between the burner and the flask, but afterwards the naked flame is employed, the heat being so regulated that from two to two and a half cubic centimetres of distillate pass over per minute. In this way fractions differing from each other in boiling-point by 50°, 25°, or 20° C. can be obtained. As soon as the requisite temperature (150° C. for the first fraction) is attained, the lamp is withdrawn until the temperature has fallen at least 20° C., when the oil is reheated to the boiling-point and again cooled, this process being repeated until no more distillate is obtained. The oil is then heated to the next boiling-point, and the cooling and reheating process repeated, and so on. In this way results can be obtained with not more than a variation of one per cent. even in the hands of different observers. In practice the fractions up to 150° C. are added together for the light naphtha or benzine, those between 150° C. and 300° C. for the burning oil, and those above 300° C. for lubricating oils and residuum.



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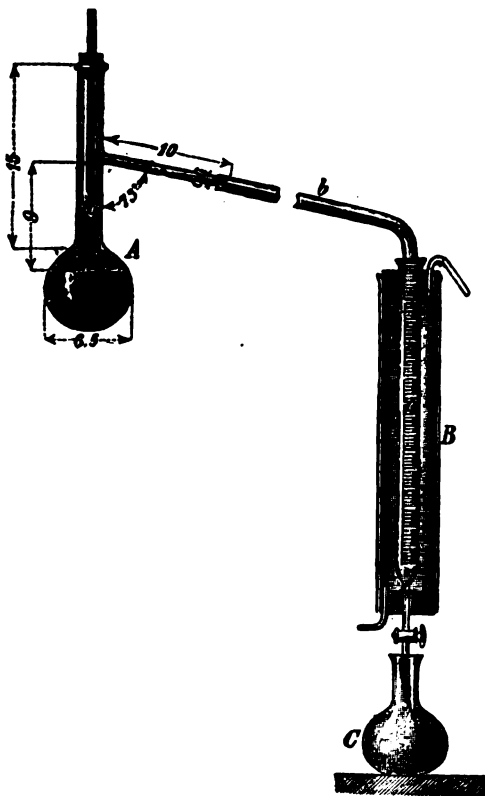

3. For Petroleum Products.—For commercial petroleum products, which are, of course, mixtures of hydrocarbons, the boiling-point becomes of only secondary importance, while, with reference to their uses as illuminants, the element of safety comes into consideration, so that what is called "flash point" and "burning point," together included in what is known as "fire-test," becomes important. For lubricating oils, the consistency or body determined in the viscosity-test and the "cold-test," or point to which they can be chilled without separating paraffine, are important. For paraffine and solid products the melting-point and amount of oil enclosed are important. And for all classes the color is a not unimportant gauge of purity. So that the analytical tests for petroleum products may be summed up under the following heads:

Specific gravity.
Fire-test, including flash-point and burning point.
Cold-test.
Viscosity.
Melting point.
Compression-test.
Colorimetric tests.

(*a*) *Specific Gravity Determinations.*—While, of course, the methods of the specific gravity bottle and the specific gravity balance are available, the determinations are, in the case of the liquid petroleum products, almost universally made with hydrometers, and these may be of two kinds, either graduated so that specific gravities are read off direct in decimal fractions less than one, or graduated in the arbitrary scales of Beaumé, Brix, Gay-Lussac, or Twaddle, the relations of which to simple fractional specific gravity numbers is known. In America and Russia the Beaumé scale is universally adopted; in Germany, the Brix spindle is used officially by customs officers; in France, the Gay-Lussac; and in England, the Beaumé scale for liquids lighter than water, and the Twaddle for liquids heavier than water. For the formulas for conversion of readings of these scales into specific gravity figures and for a complete table of Beaumé degrees in comparison with the corresponding specific gravity figures, see Appendix. The use of direct specific gravity hydrometers is gradually extending, especially in Germany, as they do away with the necessity of all reduction tables. The specific gravity tables for liquids lighter than water are calculated for a temperature of 60° F., and in practice it is customary to add to or subtract from the observed specific gravities .004 for every 10° F. above or below 60° F., and this is found to afford a sufficiently close approximation to the truth for all commercial purposes in the case of all the ordinary petroleum products.

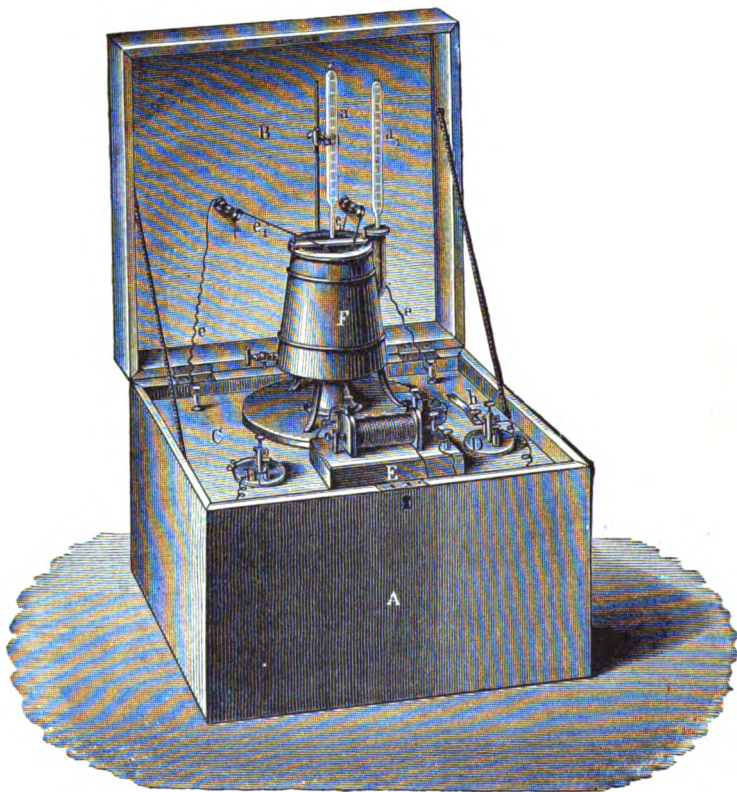
(*b*) *Fire-test.*—Just as crude petroleum is dangerous because of the dissolved gases, although its specific gravity may be relatively high, so illuminating oils may give off, at temperatures far below their boiling-point, small amounts of inflammable vapors, which might make these oils dangerous for use in lamps where the oil reservoir gradually becomes warm. A distillate may have vapors of higher and lower boiling-point carried over with it. Two points may be determined with a petroleum oil, the *flashing point*, or the temperature at which the oil gives off vapors which, mixing with air, cause an explosion or flash of flame, dying out, however, at once, and the *burning point*, or the temperature at which a spark or lighted jet will ignite the liquid itself, which then continues to burn. The

later point is usually 6° to 20° C. higher than the former, but there is no fixed relation between them. The danger, of course, begins when an oil will flash, so the flash-point is generally taken as the basis of legal prescription; Austria and the New York Produce Exchange alone recognize formally the burning-test instead of the flash-test. Most European countries and most of the States in the United States prescribe a flash-test. The United States have no national regulation on the subject.

The different forms of apparatus in use to determine the safety of oils are based upon either one of two principles,—the direct determination of flash or burning point, or the determination of the increased tension of vapor which the oil shows as the temperature rises. The second class is represented by a single form of apparatus, that of Salleron-Urbain, used to some extent in France; the first class is represented by a dozen or more different forms, chiefly of American, English, and German invention. The earliest form, that of the Tagliabue open-cup tester, is shown in Fig. 7, in which the glass cup *D*, holding the oil to be tested, is heated by the water-bath *A*. When the thermometer, the mercury of which is just immersed, indicates 90° F. (32° C.), the spirit lamp is withdrawn and the temperature allowed to rise more slowly to 95° F. (35° C.), when a lighted splinter of wood is passed to and fro over the surface of the oil. If the gas rising from the oil does not ignite, the water-bath is heated again and tests are made when the thermometer indicates 100° F. (38° C.), 104° F. (40° C.), and 108° F. (42° C.). A flash at 108° F. is considered as marking the oil at 110° F. flash-test. This form was the first one officially adopted in the United States, and is still used somewhat in Germany and Austria. The New York Produce Exchange and the American petroleum inspectors have now adopted an open-cup tester, known as the Saybolt tester, in which the electric induction-spark is made to pass over the top of the open oil-cup. It is shown in Fig. 8. *F* is a water-bath, the

Fig. 7.

temperature of which is noted by an independent thermometer. Although this was a decided improvement on the first Tagliabue apparatus, it was found that, like the other open-cup apparatus, it gave readings which were variable and higher than if the top of the cup were covered. This led to the study of the whole subject by Sir Frederick Abel, at the request of the English government, and the adoption by the English government as their official standard of the Abel tester. This has since been adopted by the German government as well, and is considered by many to be the most exact now in use. It is shown in Fig. 9. The following is a description of the details of the apparatus: "The oil-cup consists of a

FIG. 8.

cylindrical vessel, two inches in diameter, two and two-tenths inches high (internal), with outward projecting rim five-tenths inch wide, three-eighths inch from the top, and one and seven-eighths inches from the bottom of the cup. It is made of gun-metal or brass (17 B. W. G.), tinned inside. A bracket, consisting of a short, stout piece of wire, bent upward, and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is one and a half inches. The cup is provided with a close-fitting, overlapping cover, made of brass (22 B. W. G.), which carries the thermometer and test-lamp. The latter is suspended from two supports from the side by means of trunnions,

upon which it may be made to oscillate; it is provided with a spout, the mouth of which is one-sixteenth of an inch in diameter. The socket which is to hold the thermometer is fixed at such angle, and its length is so adjusted, that the bulb of the thermometer, when inserted to full depth, shall be one and a half inches below the centre of the lid. The cover is provided with three square holes, one in the centre, five-tenths inch by four-tenths inch, and two smaller ones, three-tenths inch by two-tenths inch, close to the sides and opposite each other. These three holes may be closed and uncovered by means of a slide moving in grooves and having perforations corresponding to those on the lid. In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide and tilted in such a way as to bring the end of the spout just below the surface of the lid. Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position." Not only are all the dimensions of parts in the Abel apparatus prescribed most minutely, but the method of carrying out the test must be followed in minute particulars in order to get accurate results. The opening and closing of the slide must be regulated either by a seconds pendulum or, as in the official German apparatus, by exact clock-work. It gives a flash-test which, on the average, is 27° F. lower than that of the open-cup apparatus, so that 73° F. Abel test is taken as the equivalent of 100° F. open-cup test.

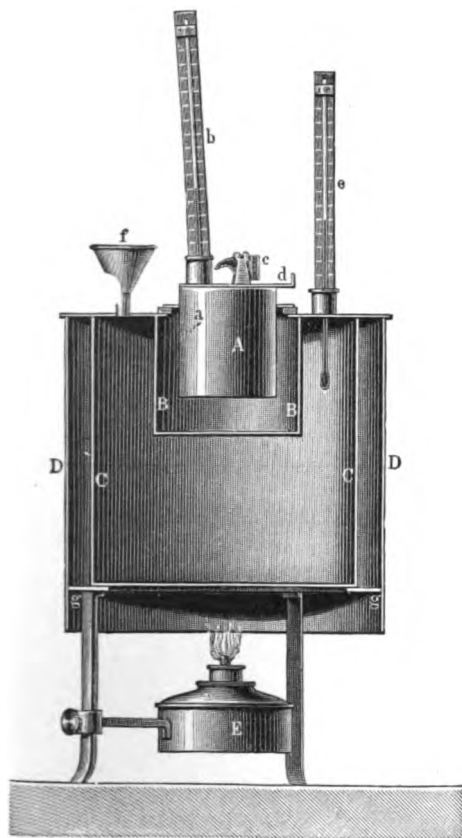



FIG. 9.

A German apparatus, which seems to be fully as exact, and simpler in its construction and operation, is Heumann's tester, shown in Fig. 10. In it the results are to a considerable degree independent of the dimensions of the oil-cup, size of flame, temperature of the water, etc. This apparatus shows to what temperature a specimen of petroleum must be heated through and through in order that the vapor given off may suffice to make an explosive mixture with a volume of air exactly equal to the volume of oil. The glass oil-vessel, *g*, is set direct in the metallic water-bath, *b*, and is exactly half-filled with oil with the aid of a measure accompanying the instrument. The agitating paddles, *c*, agitate the oil and the air-and-vapor mixture independently. The little flame or lamp for igniting the explosive mixture is attached to a button at *d*, and here is a small hole through which the gas-and-air mixture escapes,

and, when ignited, yields a flame about five millimetres high. In making the test, after agitation of the mixture, the button, *k*, is pressed down until the little flame is pushed below the surface, when, if the temperature of flashing has been reached, it ignites the explosive mixture of air and vapor, and is blown out in turn by the slight puff of the explosion. The apparatus is said to give results agreeing perfectly with those gotten with the more complicated but official Abel tester. Other forms of apparatus are those of Engler (a closed test apparatus with the Saybolt electric spark attachment), of Parrish, used in Holland, and of Bernstein.

Victor Meyer first adopted the principle that the true flash-point of a petroleum is that temperature at which air, shaken with petroleum, can be ignited by a small flame, and proposed the thorough agitation of the warmed oil to be tested with air before applying the flame. The simplest form of apparatus in which this principle is applied is the flash-tester of Stoddard, shown in Fig. 11. The air-current escapes from a fine-drawn opening in the glass tube, and must raise a foam several millimetres in height on the surface of the oil. The cylinder containing the oil may be a small Argand lamp-chimney, and the whole apparatus is lowered into a water-bath. The little jet of flame is passed to and fro over the opening at the top of the chimney, while the thermometer, immersed in the oil, is read.

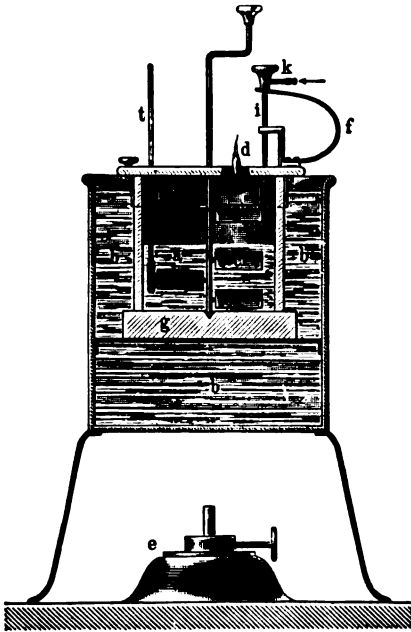
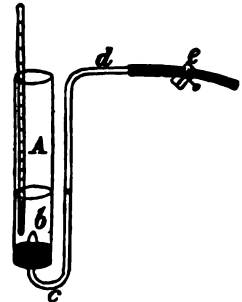



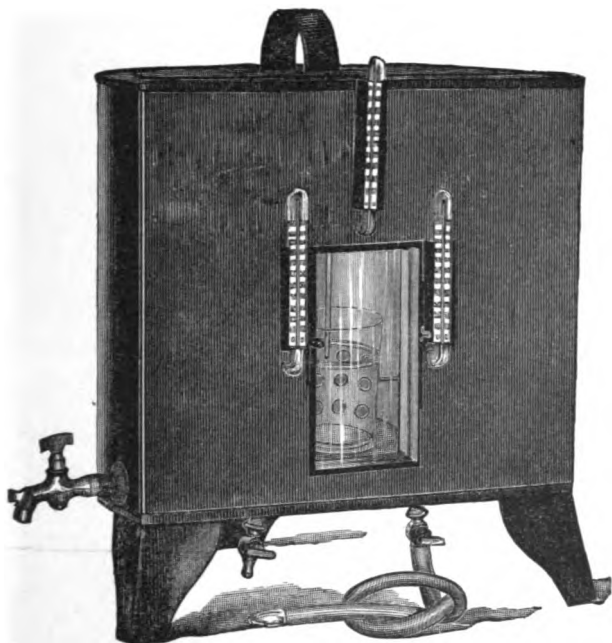
Fig. 10.

Fig. 11.

(*c*) *Cold Test.*—This is applied chiefly to lubricating oils. The execution of it with Tagliabue's standard oil-freezer is shown in Fig. 12. The glass oil-cup, four inches in depth and three inches in diameter, is adjusted to a rocking shaft, seen at the side of the cup, so as to show by its motion whether the oil is congealing or not. Surrounding the oil-cooling chamber is the ice-chamber, and outside of this is a non-conducting jacket filled with mineral wool. Three thermometers are used: one in the oil-cup and the other two in the ice-chamber to either side. Two stopcocks below, communicating with the cooling-chamber, allow of the forcing in of warm atmospheric air to raise the temperature within when necessary. A glass door in the side opposite the oil-cup allows of the reading of the ther-

mometer without opening the cooling-chamber. The cold-test is also frequently applied by simply taking the oil in a sample bottle, the diameter of which is about one and a half inches, chilling it in a freezing mixture, and noting the temperature at which, on inclining the tube, the oil no longer flows, or that at which the separation of paraffine commences.

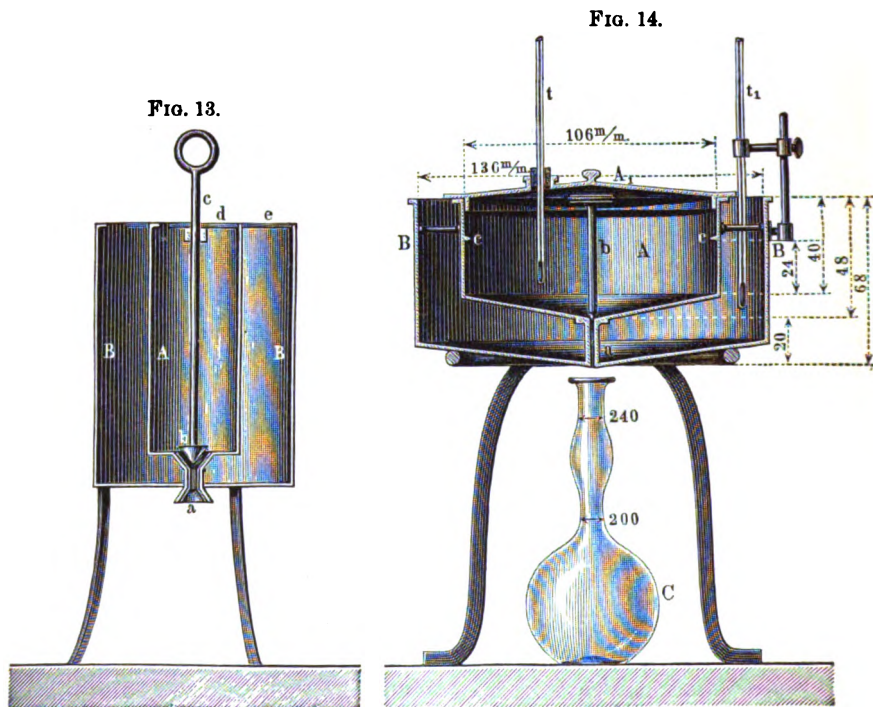
(*d*) *Viscosity Test.*—As before stated, the "viscosity" or body of a lubricating oil is one of its most important characters. Its determination is, therefore, to be made with great care. The earlier forms of apparatus consisted simply of glass tubes, of pipette form, which, being filled with oil to a certain mark, were allowed to empty while the time was accurately noted. The pipette was set in a hot-water funnel or similar vessel, and

FIG. 12.

the water in this outer vessel brought to 60° F., so that the observation on the oil might be at a standard temperature.

Other forms are those of Coleman, Mason, and Redwood, in England, and F. Fischer and C. Engler, in Germany. The Redwood viscosimeter, a very accurate instrument, will be found described and illustrated fully in "Allen's Commercial Organic Analysis" (2d ed., vol. ii. p. 198). The Fischer viscosimeter is shown in Fig. 13. The outer vessel, *B*, having been filled with warm water, the oil-vessel, *A*, has placed in it about sixty-five cubic centimetres of the oil sample, filling it to a mark on the inside. When the thermometer, immersed in the oil, shows the proper temperature, fifty cubic centimetres are allowed to run into a graduated flask placed below and the time required for its flow noted. The exit-tube, *a*, consists of a platinum tube 1.2 millimetres wide and 5 millimetres long, which is surrounded by a wider copper tube. This exit-tube is enlarged conically at either end,

above to allow of the closing by the conical plug, *b*, and below to allow of better flow of the escaping oil. In the Engler instrument, illustrated in Fig. 14, still greater care is taken to insure accurate measurement of the volume of oil operated upon, and that it shall flow under exactly similar conditions in comparative tests. Two hundred and forty cubic centimetres of water fill the inner vessel just to the mark *c*, and when the temperature of 20° C. (68° F.) is reached, two hundred cubic centimetres are run out into the vessel below. The oil to be tested is similarly filled in to the mark, and when the temperature 20° C. is reached, after keeping the oil at this for some three minutes, the plug, *b*, is withdrawn, and two hundred cubic centimetres are run into the vessel below, while the time required is accurately

Fig. 13.

Fig. 14.

noted. This time in seconds, divided by the time in seconds required for the running of the same volume of water, gives the specific viscosity or viscosity-grade, as Engler terms it.

The lubricating value of oils can be determined best by actual use upon the surfaces where friction is felt, and instruments to determine such value are, therefore, based upon experimental trials of the diminution of friction on moving surfaces, when covered by the oils to be compared. Such an instrument is the well-known Thurston lubricating oil-tester, shown in Fig. 15, in which both the resistance in the speed of revolution of a rotating axis due to friction and the heating of the axis and the bearing in which it rotates are measured.

(*e*) *Melting Point.*—The "melting point" of paraffine should rather be called the congealing point, as what is taken usually is the temperature at which the sample, after having been melted, and while in the process of cool-

ing, begins to solidify. The American test is conducted by melting sufficient of the samples to three-fourths fill a hemispherical dish three and three-fourths inches in diameter. A thermometer with a round bulb is suspended in the fluid so that the bulb is only three-fourths immersed, and the material being allowed to cool slowly, the temperature is noted at which the first indication of filming, extending from the sides of the vessel to the thermometer bulb, occurs. The English test is made by melting the sample in a test-tube about three-quarters of an inch in diameter, and stirring it with a thermometer as it cools, until a temperature is reached at which the crystallization of the material produces enough heat to arrest the cooling, and the mercury remains stationary for a short time. The results afforded by this test are usually from 2½° to 3° F. lower than those furnished by the American test. The melting point is also sometimes determined by observing the temperature at which a minute quantity of the sample previously fused into a capillary tube, and allowed to set, becomes transparent when the tube is slowy warmed in a beaker of water.

Fig. 15.

(*f*) *Compression Test.*—Paraffine scale usually contains oil and sometimes water. The percentage of oil is determined by subjecting a weighed quantity of the material to a given pressure for a specified time and noting the loss in weight. The test is made at 60° F., the quantity of material employed five hundred grains, the pressure is nine tons over the whole surface of the

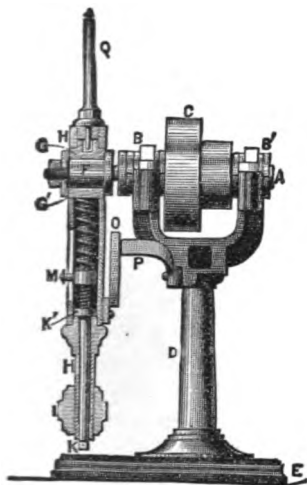
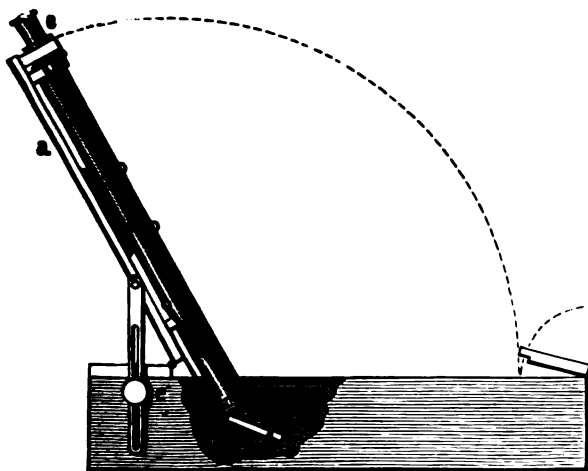
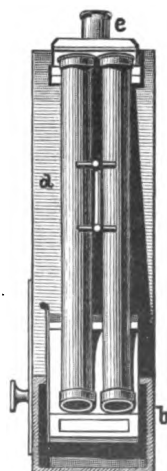



Fig. 16. Fig. 17.

circular press-cake, five and five-eighths inches in diameter, and this pressure is maintained for five minutes, the oil expressed being absorbed by blotting-paper.

(*g*) *Colorimetric Tests.*—The color of petroleum oil is determined in the United States (as regards oil for export), in England, and in Russia (in the case of oil for export) mainly by the use of the Wilson chromometer. In Germany they use both a modification under the name of the Wilson-Ludolph chromometer and Stammer's colorimeter. The Wilson instrument, shown in Fig. 16 and Fig. 17, is fitted with two parallel tubes, furnished with glass caps, and at the lower end of the tubes is a small mirror by means of which light can be reflected upward through the tubes with an eye-piece. One of these tubes is completely filled with the oil to be tested, and beneath the other tube, which remains empty, is placed a disk of stained glass of standard color. On adjusting the mirror and looking into the eye-piece the circular field is seen to be divided down the centre, each half being colored to an extent corresponding with the tint of the oil and of the glass standard respectively. An accurate comparison of the two colors can thus be made. The glass disks, which for the English trade are of five shades of color, termed good merchantable, standard white, prime white, superfine white, and water white, are issued by the Petroleum Association of London. In Germany, the Bremen Exchange recognizes seven shades of color,—straw, light straw, prime light straw to standard white, prime light straw to white, standard white, prime white, and water white.

In addition to these special tests there may be mentioned a general method recently devised by A. Riche and G. Halphen (*Journ. Pharm. Chem.*, 1894, xxx. 289) for determining whether a petroleum distillate has been obtained from American or Russian crude petroleum, and for distinguishing crude petroleum from mixtures of petroleum distillate and residuum. The process consists in the gradual addition by means of a burette of a mixture of equal volumes of anhydrous chloroform and ninety-three per cent. alcohol to four grammes of the sample of the oil until solution is effected and the liquid becomes clear. It was found that samples of crude petroleum required much more of the solvent to produce a clear liquid than fractions of the same density obtained by distillation, and that the higher boiling fractions of American petroleum required a larger quantity of the solvent than sufficed for the Russian product of corresponding specific gravity.

3. For Ozokerite.—The physical tests are the same as those for paraffine scale.

4. For Asphalts.—When asphalts and bitumens are to be used for varnish-making, the determination of the total bitumen soluble in carbon disulphide or oil of turpentine suffices. When, on the other hand, the asphalt is to be considered with reference to its value for asphalt paving purposes, it is necessary to examine into the quality of the bitumen. For this purpose the total bitumen (amount soluble in carbon disulphide), organic non-bitumen, and ash are first determined. Then the amount of bitumen soluble in petroleum-naphtha (so-called *petrolene*) is ascertained. The difference between this and the total bitumen is called *asphaltene*. The former of these portions is in general tough and elastic, while the latter is hard and brittle. For paving purposes the asphalt should contain an excess of petrolene over asphaltene. Instead of petroleum-naphtha and carbon disulphide, acetone and chloroform may be used with advantage for the extractions.

The liquid asphalts or malthas sometimes contain so much material volatile at temperatures below 300° F. that the simple determination of

bitumen soluble in petroleum-naphtha would be misleading and valueless unless they were previously heated to drive off these light oils, as these volatile portions are not comparable in value with the petrolene of solid asphalts. Therefore a test is commonly made of the percentage of loss in such asphalts when heated to 300° F. or 400° F. for ten hours, and this is then taken in connection with the extraction tests.

## V. Bibliography and Statistics.

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## STATISTICS.

1. For Natural Gas.—As already stated, the production of natural gas in the United States has reached a maximum and is now steadily decreasing.

*Value of Natural Gas consumed in the United States. 1893–1898.*

| Localities. | 1893. | 1894. | 1895. | 1896. | 1897. | 1898. |
|---|---|---|---|---|---|---|
| Pennsylvania | $6,488,000 | $6,279,000 | $5,852,000 | $5,528,610 | $6,242,543 | $6,806,742 |
| New York | 210,000 | 249,000 | 241,530 | 256,000 | 200,076 | 229,078 |
| Ohio | 1,500,000 | 1,276,100 | 1,255,700 | 1,172,400 | 1,171,777 | 1,488,308 |
| West Virginia | 123,000 | 395,000 | 100,000 | 640,000 | 912,528 | 1,334,023 |
| Indiana | 5,718,000 | 5,437,000 | 5,203,200 | 5,043,635 | 5,009,208 | 5,060,969 |
| Other States | 307,250 | 318,300 | 354,220 | 361,867 | 290,290 | 377,693 |
| Total | $14,346,250 | $13,954,400 | $13,006,650 | $13,002,512 | $13,826,422 | $15,296,813 |

(Mineral Resources of the United States for 1898.)

2. For Petroleum.—The production of petroleum in the United States during the past five years, according to "Mineral Industry of the United States for 1899," is as follows:

| | Barrels (42 gal.). | Metric tons. | Value at place of production. |
|---|---|---|---|
| 1895 | 55,033,495 | 7,677,364 | $74,776,761 |
| 1896 | 55,254,795 | 7,708,236 | 65,753,216 |
| 1897 | 57,124,783 | 7,992,046 | 44,914,360 |
| 1898 | 51,774,465 | 7,243,509 | 42,100,522 |
| 1899 | 54,048,100 | 7,566,734 | 62,911,637 |

The distribution of this production over the different States for the years 1894–99 is thus shown on the same authority:

| State. | 1894. | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|---|
| | Barrels. | Barrels. | Barrels. | Barrels. | Barrels. | Barrels. |
| Appalachian field | 30,622,336 | 30,406,693 | 33,455,571 | 34,724,700 | 31,100,360 | 33,158,664 |
| Ohio (Lima field) | 13,891,795 | 18,415,631 | 15,362,176 | 15,307,376 | 13,377,590 | 13,443,425 |
| Indiana (Lima field) | 3,688,666 | 4,386,132 | 4,659,290 | 4,353,138 | 3,751,307 | 3,772,011 |
| Colorado | 803,000 | 530,000 | 400,000 | 650,000 | 650,000 | 600,000 |
| California | 600,000 | 1,245,339 | 1,257,780 | 1,911,569 | 2,249,088 | 2,365,000 |
| Texas | none. | none. | none. | 65,000 | 544,620 | 600,000 |
| Other States | 44,300 | 49,300 | 119,478 | 113,000 | 101,500 | 109,000 |
| Total | 49,650,097 | 55,033,095 | 55,254,295 | 57,124,783 | 51,774,465 | 54,048,100 |

The exportation of crude oil and the various products therefrom for the years 1894–98 is shown in the annexed table from the authority last quoted, p. 537:

| Year ending Dec. 31st. | Mineral crude (all gravities). | | Naphthas, benzine, gasolene, etc. | | Illuminating oils. | |
|---|---|---|---|---|---|---|
| | Gallons. | Dollars. | Gallons. | Dollars. | Gallons. | Dollars. |
| 1894 . . | 114,269,000 | 4,617,000 | 14,832,000 | 904,000 | 726,727,000 | 29,799,000 |
| 1895 . . | 116,108,000 | 6,286,000 | 12,922,000 | 1,000,000 | 686,006,000 | 43,540,000 |
| 1896 . . | 118,133,000 | 6,082,000 | 13,641,000 | 1,123,000 | 758,076,000 | 49,704,000 |
| 1897 . . | 121,864,000 | 5,044,000 | 13,704,000 | 1,020,000 | 804,446,000 | 46,896,000 |
| 1898 . . | 120,436,000 | 5,019,000 | 17,255,000 | 1,071,000 | 764,823,000 | 38,895,000 |

| Year ending Dec. 31st. | Lubricating and heavy paraffine oils, etc. | | Residuum and tar, pitch, etc. | | Total. | |
|---|---|---|---|---|---|---|
| | Gallons. | Dollars. | Gallons. | Dollars. | Gallons. | Dollars. |
| 1894 . . | 88,975,000 | 5,137,090 | 119,000 | 10,000 | 894,922,000 | 44,468,000 |
| 1895 . . | 47,876,000 | 6,239,000 | 170,000 | 15,000 | 863,082,000 | 57,181,000 |
| 1896 . . | 51,705,000 | 6,770,000 | 521,000 | 28,000 | 942,076,000 | 63,657,000 |
| 1897 . . | 52,679,000 | 6,732,000 | 12,247,000 | 335,000 | 1,004,941,000 | 60,007,000 |
| 1898 . . | 65,526,000 | 7,626,000 | 30,436,000 | 815,000 | 998,476,000 | 53,423,000 |

According to the *Petroleum Review*, the domestic consumption of refined petroleum in 1890 reached 11,000,000 barrels; in 1891, 12,000,000 barrels; in 1892, 13,000,000 barrels; and in 1893, 14,000,000 barrels.

The exportations of paraffine and paraffine wax for the years 1895–97 have been, according to "United States Bureau of Statistics," as follows:

| | | | |
|---|---|---|---|
| 1895 . . . . . . . . . | 95,076,165 | pounds, valued at | $3,569,614 |
| 1896 . . . . . . . . . | 105,882,575 | " " | 4,406,841 |
| 1897 . . . . . . . . . | 126,865,128 | " " | 4,957,096 |

Closely connected with the oil-fields of the United States are those of Canada. The production and value of Canadian petroleum for the years 1894–99 are, according to "The Geological Survey of the Dominion of Canada," as follows:

| | Production in barrels of 35 imperial gallons. | Value. |
|---|---|---|
| 1894 . . . . . . . . . . . . . . . | 829,104 | $835,322 |
| 1895 . . . . . . . . . . . . . . . | 726,138 | 1,086,738 |
| 1896 . . . . . . . . . . . . . . . | 726,822 | 1,155,647 |
| 1897 . . . . . . . . . . . . . . . | 709,857 | 1,011,546 |
| 1898 . . . . . . . . . . . . . . . | 758,391 | 1,061,747 |
| 1899 . . . . . . . . . . . . . . . | 808,570 | 1,202,020 |

Next in importance to the oil-fields of the United States and rapidly increasing in their production are those of Russia. The total production of crude petroleum on the Apsheron peninsula and shipments of petroleum products from Baku for the years 1894–98, according to "Mineral Resources of the United States for 1898–99," p. 144, were as follows:

(1 barrel = 1.38 metric centners = 8.42 poods = 1.59 hectolitres.)

| Years. | Production. | Shipments from Baku. | | | | |
|---|---|---|---|---|---|---|
| | | Illuminating oil. | Lubricating oil. | Residuum. | Crude oil. | Total. |
| | Barrels. | Barrels. | Barrels. | Barrels. | Barrels. | Barrels. |
| 1894 . . | 37,811,773 | 8,704,156 | 782,396 | 23,667,482 | 2,102,690 | 35,256,724 |
| 1895 . . | 47,713,983 | 9,898,288 | 825,489 | 22,050,232 | 1,849,780 | 34,754,254 |
| 1896 . . | 49,633,252 | 10,569,670 | 1,084,095 | 22,616,271 | 3,117,898 | 37,511,687 |
| 1897 . . | 54,744,303 | 11,042,054 | 1,114,180 | 27,106,357 | 2,896,333 | 42,303,912 |
| 1898 . . | 60,597,544 | 11,569,804 | 1,273,961 | 29,628,484 | 5,365,770 | 48,015,281 |

Of the production of 1893, amounting to 5,320,000 tons, 1,790,000 tons were obtained from 38 fountain-springs, the remainder being pumped from wells. Of this production in 1893, 4,775,440 tons were worked up with the production of 1,402,728 tons of kerosene, 102,095 tons of lubricating oil, 4136 tons of benzine, 7758 tons of asphalt, gasolene, etc., and 2,351,240 tons of residuals. Thus, 3.41 tons of crude petroleum were used for the production of one ton of kerosene or burning oil. The residuals are now very largely used (especially in Russia) for fuel on railways, steamers, and in factories (*Journ. Soc. Chem. Ind.*, 1894, p. 1235).

The petroleum production of Galicia, the third most productive source, has been, according to Austrian official statistics quoted in "The Mineral Industry for 1898," as follows:

| | Metric tons. | Value in florins (= 40.5 cents). |
|---|---|---|
| 1893 . . . . . . . . . . . . . . . | 96,331 | 3,008,819 |
| 1894 . . . . . . . . . . . . . . . | 111,930 | 3,252,554 |
| 1895 . . . . . . . . . . . . . . . | 188,634 | 4,464,353 |
| 1896 . . . . . . . . . . . . . . . | 262,356 | 5,188,855 |
| 1897 . . . . . . . . . . . . . . . | 275,204 | 5,876,692 |

The production of crude petroleum for Roumania in recent years is thus given in "Mineral Resources of the United States for 1898–99," p. 167:

| | Barrels (42 U. S. gallons). | | Barrels (42 U. S. gallons). |
|---|---|---|---|
| 1894 . . . . . . . . . . . . | 507,254 | 1897 . . . . . . . . . . . . | 570,886 |
| 1895 . . . . . . . . . . . . | 575,200 | 1898 . . . . . . . . . . . . | 767,304 |
| 1896 . . . . . . . . . . . . | 543,348 | | |

The production in British India (chiefly Burmah) for the years 1894–97, according to the same authority (p. 162), amounted to:

| | Gallons. | Barrels (42 gallons). | Value (rupees = $0.436). |
|---|---|---|---|
| 1894 . . . . . . . . . . . . | 11,139,597 | 318,274 | 1,100,709 |
| 1895 . . . . . . . . . . . . | 13,013,990 | 371,828 | 1,542,591 |
| 1896 . . . . . . . . . . . . | 15,057,094 | 430,203 | 1,793,355 |
| 1897 . . . . . . . . . . . . | 19,128,828 | 546,538 | 2,263,772 |

The production of Germany, the only other country yielding any notable quantity, for the years 1894–98, has been, according to the same authority (p. 170):

| | Metric tons. | Value. |
|---|---|---|
| 1894 . . . . . . . . . . . . . . . | 17,232 | $233,387 |
| 1895 . . . . . . . . . . . . . . . | 17,051 | 230,989 |
| 1896 . . . . . . . . . . . . . . . | 20,395 | 285,243 |
| 1897 . . . . . . . . . . . . . . . | 23,314 | 335,147 |
| 1898 . . . . . . . . . . . . . . . | 25,789 | 378,770 |

3. FOR OZOKERITE AND NATURAL PARAFFINE.—The production of ozokerite in Galicia in recent years is thus given in "Mineral Resources of the United States for 1898–99," p. 267:

| | Metric tons. | Short tons. |
|---|---|---|
| 1893 | 5624.8 | 6198.5 |
| 1894 | 6743.1 | 7431.0 |
| 1895 | 6644.5 | 7322.0 |
| 1896 | 7210.0 | 7945.0 |

The production of Utah ozokerite (refined) has been:

| | | | |
|---|---|---|---|
| 1890 | 350,000 pounds | (158.9 metric tons), | valued at $26,250 |
| 1891 | 50,000 " | ( 23 " " ), | " " 3,000 |
| 1892 | 130,000 " | ( 59 " " ), | " " 7,800 |
| 1893 | None since. | | |

4. FOR ASPHALT AND SHALE OIL INDUSTRY.—The production of asphalt and bituminous rock in the United States in recent years has been, according to "Mineral Resources of the United States for 1898–99":

| | Short tons. | Value. |
|---|---|---|
| 1894 | 60,570 | $353,400 |
| 1895 | 68,163 | 348,281 |
| 1896 | 80,503 | 577,563 |
| 1897 | 75,945 | 664,632 |
| 1898 | 76,337 | 675,649 |

Of this 76,337 tons about 2000 tons is bituminous limestone, some 24,000 tons of various grades of liquid or solid asphaltum, and the balance is bituminous sandstone.

The importations of asphaltum of various kinds, according to "Mineral Resources of the United States for 1898–99," have been:

| | Long tons. | Value. |
|---|---|---|
| 1894 | 102,505 | $313,680 |
| 1895 | 79,557 | 210,556 |
| 1896 | 96,192 | 304,596 |
| 1897 | 115,528 | 392,770 |
| 1898 | 69,857 | 203,385 |

The estimated quantity of bituminous shale distilled in recent years in Scotland, according to Boverton Redwood ("Petroleum and its Products," vol. ii. p. 406), was:

| | |
|---|---|
| 1890 | 2,180,483 tons. |
| 1891 | 2,337,932 " |
| 1892 | 2,077,076 " |
| 1893 | 1,947,842 tons. |
| 1894 | 1,982,409 " |

The following are the figures for the German mineral-oil trade for 1892–93. Forty-eight shale-oil works were operated with 1297 ovens and 1067 workmen; 20,521,453 hectolitres of coal were distilled, and 1,195,892 centners of tar and 5,651,566 centners of coke were obtained. The tar was valued at 4,345,422 marks and the coke at 1,643,748 marks. On working up the tar there were obtained 159,250 centners of hard and soft paraffine, 102,306 centners of solar oil, and 623,691 centners of different paraffine oils. The value of the combined products was 11,098,496 marks.

# CHAPTER II.

## INDUSTRY OF THE FATS AND FATTY OILS.

### I. Raw Materials.

1. OCCURRENCE OF THE MATERIALS.—The fats and fatty oils are of both vegetable and animal origin. They occur not only widely spread through these two kingdoms of nature, but constitute often the larger proportion by weight of the material in which they are found. No part of the plant seems to be entirely wanting in fat, although that found in the leaves is more of a wax-like character than the oil obtained from the seeds and fruit; in the animal, fats are present in all tissues and organs and in all fluids with the exception of the normal urine. In plants the percentage of fat seems to be in inverse ratio to the percentage of starch and sugar, and ranges from sixty-seven per cent. in the Brazil nut to one per cent. in barley. While the oil-bearing plants are far too numerous to allow of a complete enumeration here, it will be desirable to state first the occurrence of those technically most important, and afterwards to examine those physical and chemical differences which lie at the basis of their different uses. Similarly the most important animal oils and fats will first be enumerated.

(*a*) VEGETABLE OILS, FATS, AND WAXES.—*Castor oil* (oleum ricini, ricinus-oel) is extracted by pressure or heat from the seeds of the *Ricinus communis*, originally from the East. It is a thick oil, of specific gravity .9667 at 15° C., colorless or yellowish, transparent, of mild taste, but becoming rancid on long exposure to air, miscible with alcohol and ether, and easily saponifiable. The shelled seeds yield from fifty to sixty per cent. of the oil.

*Cotton-seed oil* (oleum gossypii seminum, baumwollen-samen-oel) is obtained by pressure from the hulled seeds of the several species of *Gossypium*, or cotton-plant. The raw oil is brownish-yellow in color, somewhat viscid, of specific gravity .922 to .9306 at 15° C., and separates some palmitin at from 6° C. to 12° C. The refined oil has a straw-yellow color, or is colorless, of pleasant nutty flavor; specific gravity, .9264 at 15° C.; boils at about 600° F., and congeals at about 50° F. for summer- and 32° F. for winter-pressed. Even at the ordinary temperature, cotton-seed oil deposits "stearine" on standing. The finer brands of cotton-seed oil intended for edible and culinary purposes are freed from this "stearine" by chilling or simply by allowing the oil to stand for some time in large storage tanks. It possesses slight drying properties, and is saponifiable, but is chiefly used in adulterating olive, lard, sperm, and other oils. The hulled seeds yield from eighteen to twenty per cent. of the crude oil.

*Hemp-seed oil* (oleum cannabis, hanf-oel) is obtained from the seeds of the *Cannabis sativa*, or common hemp. It has a mild odor but mawkish taste, and greenish-yellow color, turning brown with age. Its specific gravity at 15° C. is .9276. It is freely soluble in boiling alcohol. Has

weaker drying properties than linseed oil, but is used in paint and varnish manufacture and in making soft soaps. The seeds contain some thirty per cent. of the oil.

*Linseed oil* (oleum lini, lein-oel) is pressed from the seeds of the *Linum usitatissimum*, or flax-plant. The oil differs in quality according to the method of its production. By cold pressure is obtained twenty to twenty-one per cent. of a pale, tasteless oil, which is used in cooking as a substitute for lard or butter in Russia and Poland. By warm pressure is obtained twenty-seven to twenty-eight per cent. of an amber-colored or dark-yellow oil. It is, when fresh, somewhat viscid, but as a drying oil it gradually absorbs oxygen and becomes thick and eventually dry and hard. The specific gravity of the fresh oil is .935 at 15° C. It is used almost exclusively in the preparation of paints, varnishes, printer's ink, and "oil-cloth." (See p. 101.)

*Poppy-seed oil* (oleum papaveris, mohn-oel) is obtained from the seeds of the opium poppy by pressure, is of pale-yellow color, and slightly sweetish taste. Specific gravity, .925 at 15° C. The cold-drawn oil, the oil of the first pressing, is almost colorless, or very pale golden yellow; this is the "white poppy-seed oil" of commerce. The second quality, expressed at a higher temperature, is much inferior, and constitutes the "red poppy-seed oil" of commerce. It is used for salads, paints, soaps, and to adulterate olive and almond oils. The seeds yield from forty-seven to fifty per cent. of oil.

*Walnut oil* (huile de noix, wallnuss-oel) is obtained from the seeds of the common walnut-tree, *Juglans regia*. The fruit to be pressed should be fully ripe and kept for several months before being pressed, as the fresh seeds yield a turbid oil. The cold-drawn oil is very fluid, almost colorless, or of a pale yellow-greenish tint, and has a pleasant smell and agreeable nutty taste; the hot-pressed oil, on the other hand, has a greenish tint and an acrid taste and smell. Walnut oil is a very good drying oil, and at least equal if not superior in that respect to linseed oil. It is chiefly used by artists for paints, as it dries to a varnish film less liable to crack than the film of linseed-oil varnish. Moreover, the better brands of walnut oil being almost colorless, it is preferred to any other oil for white paints.

*Sunflower oil* (huile de soleil, sonnenblumen-oel) is obtained from the seeds of the sunflower (*Helianthus annuus*), and is a limpid pale-yellow oil of mild taste and pleasant smell. Specific gravity, .925 at 15° C. It belongs to the class of drying oils, but dries more slowly than linseed oil. The cold-drawn oil is also used in Russia for culinary purposes, while that expressed at a higher temperature is employed in soap-making and for the manufacture of varnishes.

*Almond oil* (oleum amygdalæ, mandel-oel) is the fixed oil obtained from both the sweet and the bitter almond The former contains the more oil, but the latter is cheaper, and the residual cake can be utilized for the preparation of the essential oil of bitter almonds. The oil is odorless, agreeable to the taste, and of yellow color. Specific gravity, .919 at 15° C. It is used in pharmacy and medicine and in soap-making.

*Corn oil* (maize oil, mais-oel) is obtained from the seeds of the maize or Indian corn, either by expressing the seed before it is employed for the manufacture of starch, or, where the corn has been fermented for the production of alcohol, by recovering it from the residue of the fermentation vats. Prepared by the former process, it is of a pale-yellow or golden-

yellow color, whereas the oil obtained by the latter process is reddish brown. Specific gravity, .921 to .924 at 15° C. The oil has slight drying properties only. It is used as a burning and lubricating oil and for soap-making. It is also employed in place of cotton-seed oil for the adulteration of lard.

*Sesamé oil* (gingili oil, teel oil, sesam-oel) is obtained from the seeds of the *Sesamum orientale* and *Sesamum indicum.* The oil possesses a yellow color, is free from odor, and has a pleasant taste. The cold-drawn oil is therefore considered equal to olive oil for table use. It has very slight drying properties. Specific gravity, .923 at 15° C. In addition to its use as an edible oil, the inferior grades are used in soap-making and as burning oil.

*Ben oil* (oleum balatinum, behen-oel) is obtained by expression from the seeds of the several species of *Moringia.* Colorless, odorless oil, not readily turning rancid. It is used by perfumers for extracting odors and for lubricating clocks and light machinery.

*Cacao butter* (oleum theobromatis) is obtained from seeds or nibs of *Theobroma cacao.* Pure white fat, with pleasant odor and taste. Fuses at 86° F. (30° C.). Specific gravity, .945 to .952. It is used for cosmetics and for pharmaceutical preparations.

*Cocoa-nut oil* (oleum cocöis, cocos-oel) is obtained from the dried pulp (copra) of the cocoa-nut by expression. An oil of the consistency of butter, fusing at 73° to 80° F. (22.7° to 26.6° C.). When fresh, is white in color and of sweet taste and agreeable odor, but easily becomes rancid. It is easily saponified, even in the cold. It is used in the manufacture of candles and padded soaps. (See p. 64.)

*Colza and rape oils* (oleum brassicæ, oleum rapæ) are practically identical. They are extracted from the several varieties of *Brassica campestris.* The seeds are called cole-seed or rape-seed. The term "colza oil" is generally applied to refined rape oil. The crude oils are used as lubricating oils, and are of dark, yellow-brown color. Refined and freed from albumen and mucilage, they become bright-yellow. The specific gravity of the refined oil is .9132 at 15° C. Rape oil is used for lamps, for lubricating machinery, and for adulterating both almond and olive oils.

*Olive oil* (oleum olivarum, oliven-oel) is expressed from the fruit of *Olea Europæa.* It differs greatly in quality according to the method by which it is obtained. The purest is nearly inodorous, pale-yellow, with pure oily taste. Specific gravity, .918 at 15° C. Does not decompose or become rancid easily, and congeals at 32° F. to a granular solid mass. The percentage of oil amounts to thirty-two per cent., of which twenty-one per cent. is furnished by the pericarp, and the remainder, which is inferior, by the seed and woody matter of the fruit. It is used extensively as an article of food or condiment, in pharmacy, as an illuminant and lubricant, and in soap-making. The lowest grade, "tournant oil," has a high per cent. of free fatty acids and readily emulsifies with sodium carbonate solution.

*Arachis oil* (peanut oil, erdnuss-oel). This oil is obtained from earth-nuts, the seeds of *Arachis hypogæa.* The cold-drawn oil of the first expression is nearly colorless, and has a pleasant taste resembling the flavor of kidney beans. Specific gravity, .917 at 15° C. The best qualities of the oil are used for table oil and the inferior grades for soap-making.

*Palm oil* (oleum palmæ, palm-oel) is obtained from the fruit of several species of palm. The fresh palm oil has an orange-yellow tint, a sweetish taste, and an odor resembling violets. Its specific gravity is about .968. Its consistency is that of butter or lard. It ordinarily becomes rancid

rapidly, and hence usually contains free acid. It is used in candle- and soap-making, and also to color and scent ointments, pomades, soap, powders, etc.

*Carnauba wax* is obtained from the leaves of the carnauba palm, *Copernicia cerifera* of Brazil. Its specific gravity is .999 and its melting point 185° F. (84° C.). It is brittle and of yellowish color. It is extensively used in the manufacture of candles.

*Japan wax* is obtained by boiling the berries of several trees of the genus *Rhus*, from incisions in the stems of which flows the famous Japan lacquer varnish. It is properly a fat, as it consists almost entirely of glyceryl palmitate. Its specific gravity is .999 and melting point 120° F. (49° C.). When freshly broken, the fractured surface is almost white or slightly yellowish-green and the odor tallow-like. It is used for mixing with beeswax in the manufacture of candles and in the manufacture of wax-matches.

*Myrtle wax*, a solid fat obtained by pressure from the berries of *myrica cerifera*. Specific gravity 1.005 at 15° C.; fusing point 45° to 46° C. It is used as a substitute for beeswax and particularly in candle-making.

(*b*) ANIMAL OILS, FATS, AND WAXES.—*Neat's-foot oil.* Prepared from the feet of oxen collected from the slaughter-houses. It is a clear, yellowish oil of specific gravity .916 at 15° C. It does not congeal until below 32° F., and is not liable to become rancid. Of great value as a lubricant, and used for softening leather and grinding of metals.

*Butter fat* is the oily portion of the milk of mammalia, but in practice the term is restricted to that obtained from cows' milk. The pure fat constitutes from eighty-five to ninety-four per cent. of the finished butter. The pure fat has a specific gravity of .910 to .914, and its melting point varies from 85° to 92° F. For fuller account of manufactured butter, see under milk (p. 254).

*Lard and lard oil* (adeps, schweine-schmalz) is the fat of the pig melted by gentle heat and strained. The crude lard is white, granular, and of the consistency of a salve, of faint odor and sweet, fatty taste. Its specific gravity is .938 to .940 at 15° C. Exposed to the air it becomes yellowish and rancid. When pressed at 32° F., it yields sixty-two parts of colorless lard oil and thirty-eight parts of compact lard. The lard is used in cooking, the lard oil for greasing wool, as a lubricant and an illuminant.

*Tallow and tallow oil* (sevum, talg). Tallow is the name given to the fat extracted from "suet," the solid fat of oxen, sheep, and other ruminants. The quality of the tallow varies according to the food of the cattle and other circumstances, dry fodder inducing the formation of a hard tallow. Its melting point varies from 115° to 121° F. The best qualities are whitish, but it has in general a yellowish tint. Beef tallow contains about sixty-six per cent. of solid fat and thirty-four per cent. of olein or tallow oil; mutton tallow contains about seventy per cent. of solid fat and thirty per cent. of tallow oil. The oil is used chiefly in the manufacture of soaps and the harder tallow for candle-making.

*Bone fat* is a whitish-yellow fat obtained by boiling bones, and is used in soap-making.

*Cod-liver oil* (oleum jecoris ceselli, leberthran) is an oil ranging in color according to the method of its preparation from pale-straw to dark-brown, and of specific gravity .923 to .924 or even .930 at 15° C. The finer qualities are used for medicinal purposes, the darker for tanners' and curriers' use.

*Menhaden oil* is obtained from the *Alosa menhaden*, a kind of herring. Is used for soap-making and tanning, and, when pure, as a substitute for cod-liver oil.

*Shark oil* is prepared from the livers of various species of shark. It is the lightest of the fixed oils, the specific gravity ranging from .865 to .876. It is used in the adulteration of cod-liver oil and for tanning.

*Whale oil* (train oil) is extracted from the blubber of the common or Greenland whale. Is yellow or brownish in color and of disagreeable odor. Specific gravity .920 to .931. It is used for illumination and for soap-making.

*Sperm oil* is procured from the deposits in the head of the sperm whale. In the living animal, the solid spermaceti is held in solution in the liquid sperm oil; when the liquid becomes cold the spermaceti separates out. The oil is very limpid, relatively free from odor, and burns well in lamps. Specific gravity, .875. It is used as a lubricant on account of its low cold test and its viscosity, and as an illuminant.

*Spermaceti* (cetaceum, walrath) is the solid wax separated out from the accompanying oil. It is yellowish at first, but when purified is white, brittle, and scaly. Its specific gravity is .943 at 15° C.; melting point, 43° to 49° C. It is only slightly soluble in alcohol, benzene, and petroleum-ether, but easily soluble in ether, chloroform, and carbon disulphide. It is used in the manufacture of candles and in pharmaceutical preparations.

*Wool grease* (woll-fett, lanolin, or *adeps lanæ*). Sheep's wool contains a large amount of fatty matter of a peculiar character. It contains free fatty acids, esters of cholesterol and isocholesterol, and the free alcohols just named. When purified from fatty acids it yields lanolin, which has the property of taking up large quantities of water in an emulsion, and is used extensively in medicine. The esters are true waxes and not glycerides.

*Beeswax* (cera flava, bienenwachs) is the substance of which the cells of the honey-bee are constructed. The crude melted wax is a tough, compact mass of yellow or brownish color, granular structure, faint taste, and honey-like odor. When bleached it becomes white. Specific gravity .959 to .969; melting point 62° to 64° C. It is used in making candles, ointments, and pomades.

*Chinese wax* (insect wax) is deposited by an insect, *Coccus cerifera*, upon the Chinese ash-tree. It is a white, very crystalline, and brittle wax, resembling spermaceti in appearance. Specific gravity .973 at 15° C.; fuses at 82° to 83° C. It is slightly soluble in alcohol and ether, very soluble in benzene. It is used in candle-making.

2. PHYSICAL AND CHEMICAL CHARACTERS OF THE DIFFERENT OILS AND FATS.—(*a*) *Physical Properties.*—Most of the vegetable fats are liquid at ordinary temperatures, because of the relatively high percentage of olein they contain. Cocoa-nut oil, palm oil, cacao butter, and a few others have a buttery consistence on account of the palmitin present. The fats of animals feeding on straw and hay are solid, because of the stearin present; the fats of carnivorous animals are all softer; the fat of fishes is liquid at ordinary temperatures, and somewhat differently constituted chemically. The solid waxes, both vegetable and animal, are in general differently constituted from the softer fats.

The fats and oils are almost insoluble in water (if the water contains albumen, gum, or alkaline carbonates in solution they readily form an

emulsion with it on shaking); alcohol only dissolves them sparingly; ether, carbon disulphide, chloroform, benzene, turpentine oil, fusel oil, and acetone dissolve them readily.

On exposure to the air, the fats, and particularly the fatty oils, absorb oxygen. The heat developed by this oxidation at times suffices to inflame wool and cotton tissues soaked with the oil. The oils which absorb oxygen in this way become thick, and finally dry to translucent resinous masses. Such oils are called "drying oils," and are used in painting and varnish-making. (See p. 101.) The specific gravity of all the fats and oils is less than unity, although the vegetable waxes are only very slightly less.

The boiling-points of the oils and fats cannot in general be taken as distinctive, as many of them begin to decompose when distilled under ordinary pressure. Their fusing and congealing points are more important; particularly in the case of oils used as lubricants does the latter denote the different value of the oil for use at low temperatures.

(*b*) *Chemical Composition of the Oils, Fats, and Waxes.*—The fatty oils, as distinguished from the mineral oils (see p. 13) and the volatile oils (see p. 94), belong to the class of compound ethers. They are salt-like bodies, composed of characteristic acids (oleic, palmitic, and stearic), known as fatty acids, in combination with an alcohol or base. In most cases the base is the triatomic alcohol glycerine, so that the oils are said to be glycerides of the several fatty acids. Some few, known as waxes, do not contain glycerine, but a monatomic alcohol in combination with the fatty acid. Most of the animal and vegetable fats contain the three proximate constituents, olein, palmitin, and stearin, the combinations of oleic, palmitic, and stearic acids respectively with glycerine. In the more liquid oils the olein predominates, in the more solid palmitin or stearin. The so-called "drying oils" contain a different acid—linoleic acid—in combination with glycerine. The fish oils contain a variety of the lower fatty acids and some solid unsaponifiable alcohols like cholesterin. The most satisfactory classification of the oils and fats is that of A. H. Allen,* which is here given in abstract.

I. *Olive Oil Group.*—Vegetable oleins. Vegetable non-drying oils. Lighter than Groups II., III., and IV. Yield solid elaidins with nitrous acid. Includes olive, almond, earth-nut, ben, rape-seed, and mustard oils.

II. *Cotton-seed Oil Group.*—Intermediate between drying and non-drying oils. Undergo more or less drying on exposure. Yield little or no elaidin. Includes cotton-seed, sesamé, sunflower, hazel-nut, and beech-nut oil.

III. *Linseed Oil Group.*—Vegetable drying oils. Yield no elaidin. Of less viscosity than the non-drying oils. Includes linseed, hemp-seed, poppy-seed, niger-seed, and walnut oils.

IV. *Castor Oil Group.*—Medicinal oils. Very viscous and of high density. Includes castor and croton oils.

V. *Palm Oil Group.*—Solid vegetable fats. Do not contain notable quantities of glycerides of lower fatty acids. Includes palm oil, cacao butter, nutmeg butter, and shea butter.

VI. *Cocoa-nut Oil Group.*—Solid vegetable fats, in part wax-like. Several contain notable proportions of the glycerides of lower fatty acids. Includes cocoa-nut oil, palm-nut oil, laurel oil, Japan wax, and myrtle wax.

VII. *Lard Oil Group.*—Animal oleins. Do not dry notably on exposure, and give solid elaidins with nitrous acid. Includes neat's-foot oil, bone oil, lard oil, and tallow oil.

VIII. *Tallow Group.*—Solid animal fats. Predominantly glycerides of palmitic and stearic acid, although butter contains lower glycerides. Includes tallow, lard, bone fat, wool fat, butter fat, oleomargarine, and manufactured stearin.

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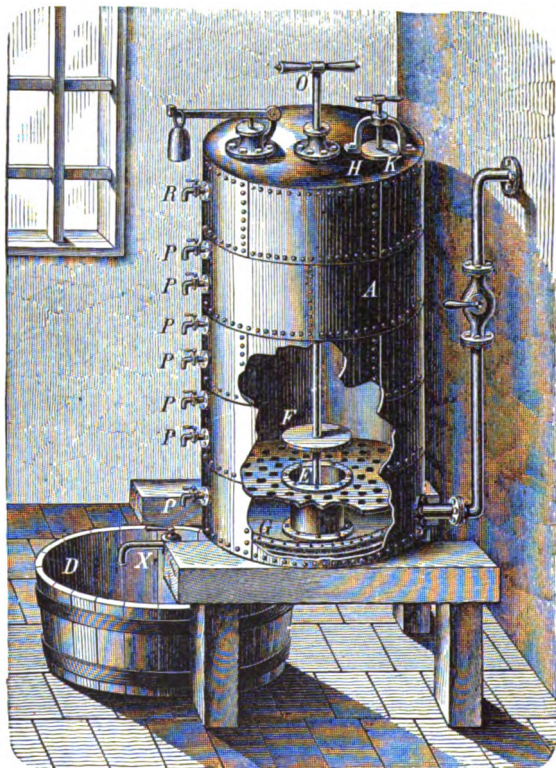
* Commercial Organic Analysis, 2d ed., vol. ii. p. 63.

IX. *Whale Oil Group.*—Marine animal oils. Characterized by offensive odor and reddish-brown color when treated with caustic soda. Includes whale, porpoise, seal, menhaden, cod-liver, and shark-liver oils.

X. *Sperm Oil Group.*—Liquid waxes. Are not glycerides but ethers of monatomic alcohols. Yields solid elaidins. Includes sperm oil, bottle-nose oil, and dolphin oil.

XI. *Spermaceti Group.*—Waxes proper. Are compound ethers of higher monatomic alcohols, with higher fatty acids in free state. Includes spermaceti, beeswax, Chinese wax, and carnauba wax.

3. Extraction of the Raw Materials and Purification of the Same.—The method of extraction of the oils and fats is, of course, determined to a considerable degree by their physical condition. Solid fats, like tallow and lard, are obtained free from the enclosing membranes by melting the finely-chopped material and drawing off the fat in the melted state;

Fig. 18.

animal oils are extracted mainly by boiling out with water; oil fruits and seeds are ground fine, and then the oil obtained by submitting the meal to pressure, either cold or with the aid of heat, or the oil is extracted by solvents like carbon disulphide and petroleum ether.

In the extraction of fats by the process of melting, three forms of procedure are followed: (1), the so-called "cracklings" process, a melting over direct fire, known, too, as the "dry melting;" (2), the melting over direct fire with the addition of dilute sulphuric acid, known as the "moist melting;" and (3), the melting by the aid of steam. In the first process, a

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little water is added and the tallow or other chopped fat is heated in open vessels. The mixture of fat globules and water at first gives it a milky appearance, but, as soon as the water is driven off, the cell membranes shrivel more and more together, forming the cracklings, and the fat appears as a clear, fused liquid. A constant stirring is required in order to prevent the fragments of membrane from sticking to the sides or bottom of the vessel and burning. The melted fat is drained from the cracklings by passing through metallic sieves, and cracklings afterwards pressed in suitable presses to recover the adhering fat, which forms a second quality tallow. A raw tallow yields on the average eighty to eighty-two per cent. of drained oil and ten to fifteen per cent. of cracklings; a very pure kidney fat will yield, however, ninety per cent. and over of drained fat.

In the second process, now generally followed, to one hundred kilos. of tallow, twenty kilos. of water mixed with one-half to one and one-half kilos. of concentrated sulphuric acid is added. The sulphuric acid attacks and destroys the cell-membranes rapidly when heated, and so allows of the liberation of the fat. In this process, as in the last, provision must be made for preventing the escape into the air of the unhealthy and offensive odors coming from the melting of the impure tallow. The escaping vapors are in part condensed and part burned under the kettles. In the third process, that of melting by steam, the steam may be directly introduced into the fat mass or indirectly used by the aid of coils of pipes.

The tallow rendering by steam is illustrated in the apparatus of Wilson, shown in Fig. 18. The steam enters through the perforated pipe *G*, under the perforated false bottom. The plate *F* having been shut down tight upon the opening *E*, the vessel is two-thirds filled with the tallow and steam applied. The pressure is allowed to rise to three and a half atmospheres (fifty-two and a half pounds per square inch) and kept at this for some ten hours. The condensed water collects under the false bottom and can be drawn off when necessary. The melted tallow is then run off from the stopcocks, *PP*, and the cracklings finally discharged through the opening *E*.

Some acid may be added to the fat or in the Evrard process, instead of acid, caustic soda, which has the advantage of combining with the noxious volatile acids evolved.

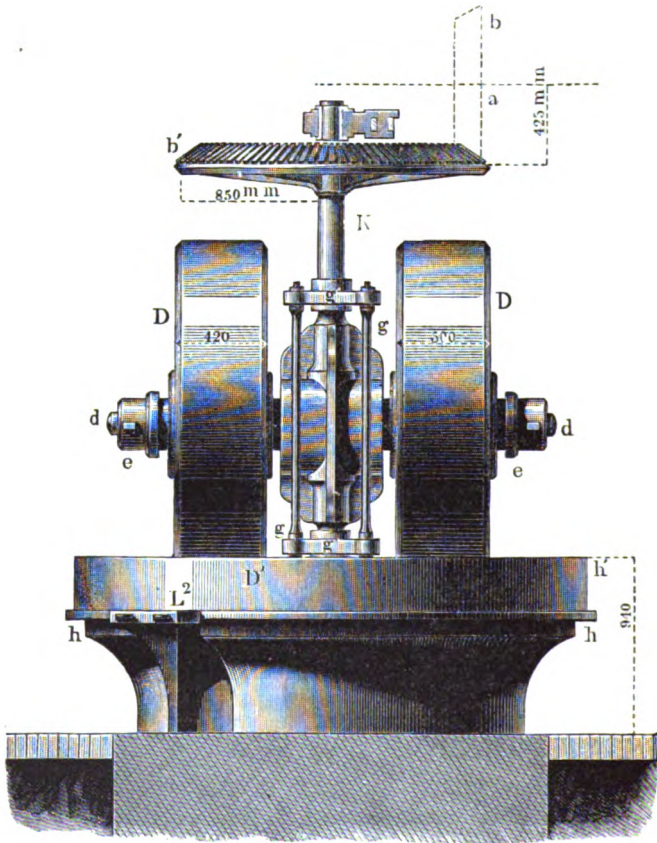
The extraction of lard takes place by similar methods to those employed for tallow, but at lower temperatures and more readily.

For the extraction of animal oils, like fish oils, the method of boiling out with water is generally employed, elevation of temperature and prolonged heating being avoided as much as possible in the case of the finer medicinal oils.

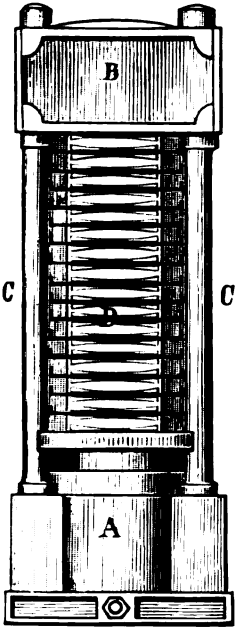
For oil-bearing fruits and seeds, the methods of obtaining oil, as already mentioned, are expression, either cold or by the aid of heat, and that of extraction by solvents.

For the expression of oils, the carefully cleansed seeds are first crushed to break the shells or kernels and then ground to fine meal. The crushing is done very generally in oil-seed mills of the construction shown in Fig. 19, where the two stones or metal wheels are made to revolve on a stone foundation on which the oil seeds are placed, and from which any excess of oil may flow. A much more perfect crushing is possible in this mill than in those in which stamps are used They are then slightly heated for the double purpose of coagulating any plant albumen and making the oil more liquid.

In the case of the best medicinal or table oils all heat is avoided and cold-pressed oils only taken. The meal is then repeatedly pressed. The result of the first pressing is often called "virgin oil," and is of better color and taste than the later lots. The pressing is done chiefly with hydraulic presses, as shown in Fig. 20, although the old wedge presses may still be used on a small scale. The crushed oil seed is placed in woolen or cotton cloths, usually covered in by bags of horse-hair, and then placed between the press-plates. The other process, that of extraction of the oil by solvents, is capable of yielding a much larger amount of oil than pressure, but has

Fig. 19.

been more or less opposed on several grounds. The solvents employed are carbon disulphide and petroleum-ether. The former is the better solvent, is used at a lower temperature, and is easily recovered from the solution afterwards without leaving any appreciable odor adhering to the oil. It, however, dissolves coloring matter and resin from the seed as well as oil, and so introduces impurity, and when not perfectly pure, it leaves sulphur impurities also in the oil. The other solvent does not dissolve so much coloring matter or resin, communicates no odor, and leaves no sulphur or other residues in the oil, and so can be used for fine table oils, if necessary. It

requires a higher temperature, however, and, condensing on the surface of water instead of under it, like carbon disulphide, requires more complicated distilling and condensing apparatus. At the present time the carbon disulphide is more generally used. The objection first urged against the extraction of oil by solvents, that they left the oil-cake valueless for cattle food because of the too complete extraction of the oil, is now met by the oil men, who leave eight to ten per cent. of fat or oil in palm-nut or other oil-cake.

Fig. 20.

The expressed or extracted oils are in many cases in quite a crude condition, containing both suspended and dissolved impurities of various kinds. To purify them for use, even in soap-making, some treatment is generally necessary. Often simple but prolonged subsidence suffices if the impurities are only suspended. Instead of subsidence, it may be necessary at times to use filtration through cotton wadding or animal charcoal. If both subsidence and filtration fail to clear the oils, it is necessary to adopt chemical treatment as the impurities in time ferment and develop a permanent rancidity or deterioration of the oil. The first process to note is that of Thénard, to add gradually one to two per cent. of sulphuric acid to oil previously heated to about 100° F. and mix by thorough agitation. The sulphuric acid both takes up the water that holds the impurities in solution and chars the impurities themselves. The treatment with acid is to be followed by a thorough washing with warm water and final filtration. Cogan's process follows the addition of sulphuric acid by that of steam. Instead of sulphuric acid, caustic alkalies are sometimes used as in the Evrard process (see p. 55), which is chiefly applied to colza and rape oils. In this case, the caustic soda saponifies a small quantity of the oil, and the soap carries down, mechanically, all impurities, leaving the oil perfectly clear. Too prolonged agitation may, however, make an emulsion of soap and oil, which separates with difficulty. R. von Wagner proposed the use of zinc chloride instead of sulphuric acid, as this chars the impurities without attacking the oil. The zinc chloride is used in concentrated solution of 1.85 specific gravity, about one and one-half per cent. being taken and thoroughly agitated with the oil. After the zinc chloride solution is withdrawn, the oil is well washed with water and filtered. Tannin is also used to clear some oils, which it effects by coagulating the albumen.

Cotton-seed oil is always colored by some resin, which is removed by treatment with alkali, which saponifies the resin and the free acids of the crude oil. A recent patent proposes to replace the sodium hydrate, which in its action causes a loss of from three to seven per cent. of the oil, by sodium carbonate, which is capable of acting upon the coloring matter, although not upon the oil. A subsequent filtration through fuller's earth is also recommended.

Still more energetic methods for purifying oils are the oxidation methods, using "chloride of lime" or bichromate of potash, and sulphuric or hydrochloric acids as applied to palm oil.

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The use of hydrogen peroxide solution has recently been tried for the bleaching of oils, with the best of results. Four or five per cent. of a ten per cent. solution will generally suffice if repeatedly shaken up with the oil to be treated.

Ozone-carriers, like ferrous sulphate solution, will also bleach in the presence of sunlight. This method is often applied with linseed oil.

## II. Processes of Treatment.

1. SAPONIFICATION OF FATS.—The composition of the proximate principle, olein, palmitin, and stearin, which make up the bulk of the fats proper, was first established by the researches of Chevreul in 1823. Their decomposition can be effected in a number of ways, by the action of bases like the alkalies and some metallic oxides, by the action of sulphuric acid liberating the fatty acids, and by the action of water alone, when aided by heat and pressure.

Chevreul at first used alkalies, patenting that process in 1825, in conjunction with Gay-Lussac, but this procedure was given up already in 1831, when Ad. de Milly replaced the alkalies by lime. This was used exclusively for a number of years, but was followed in 1854 by the independent discovery of Tilghman and Berthelot of the method of decomposing by the use of hot water superheated by high pressure. Melsens also proposed the same process substantially a little later. In consequence of the danger connected with the high temperature and pressure, this process is not carried out any longer in its original shape, but is now replaced by the "autoclave" process, mentioned later. In 1841 Dubrunfaut found that if neutral fats were treated first with sulphuric acid, and then boiled with water, the fatty acids might be distilled in an atmosphere of superheated steam without decomposition. This constituted the distillation process. It was extensively used in England. Wilson and Gwynne found it possible, with proper application of the superheated steam and regulation of the temperature (290° to 315° C.), to dispense with the sulphuric acid, and to decompose the fats and then distil them without any decomposition. This process is now used on a large scale by the Price Candle Company in England. Still later, Bock, of Copenhagen, found that if the membranous cellular tissue that enclosed the fat be decomposed by a preliminary treatment with sulphuric acid and the charred tissue, which by oxidation becomes heavier than the fat and sinks through it, be removed, the pure fat could be decomposed by boiling with water in open tanks. The separated fatty acids are so pure in color that washing suffices, and no distillation is necessary.

These several processes have been in time modified and amalgamated until now only three or four processes are practically followed on a large scale:

(1) *The saponification by alkalies* used exclusively in soap-making and yielding a soda or potash salt of the fatty acid. (See SOAPS, p. 62.)

(2) A combination of the lime and hot-water processes, known as Milly's "*autoclave process*," in which two to four per cent. of lime is made to do the work of saponification, for which 8.7 per cent. is theoretically needed, and for which fourteen to seventeen per cent. was at first used. The saponification is carried out in the presence of water in strong, closed, metallic vessels, at a temperature of 172° C. One form of such vessel for

the saponification by lime under pressure, that of Léon Droux, is shown in Fig. 21. At present the form of the vessel in use is more generally that of a sphere, which stands the eight to ten atmospheres internal pressure better. The lime soap, technically called "rock," after its separation is decomposed by sulphuric acid, four parts of acid to each three parts of lime used being taken. After the complete subsidence of the calcium sulphate the free fat acids are thoroughly washed with water and steam.

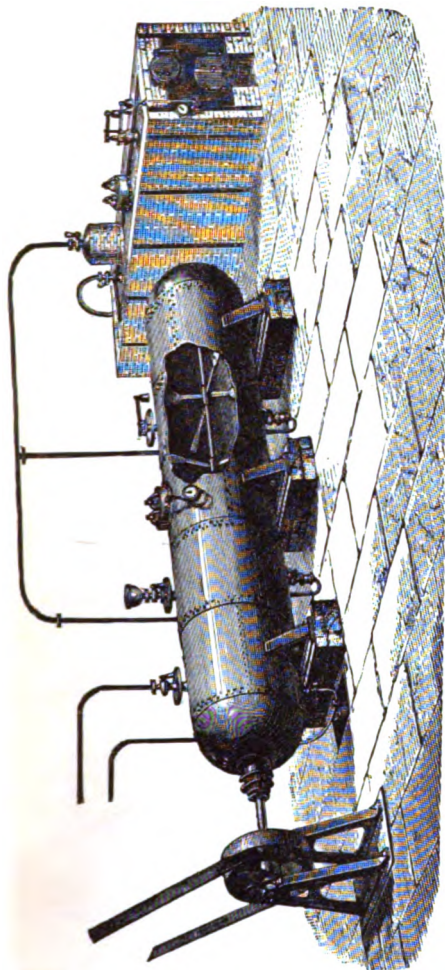



FIG. 21.

(3) *The sulphuric acid saponification*, followed by distillation. This process is almost exclusively followed in England. The amount of sulphuric acid used has gradually been diminished, as it is found that a relatively smaller percentage will suffice. For offal fats some twelve per cent. is now used, for tallow nine per cent., and for palm oil six per cent. The decomposition generally requires some hours at a temperature varying from 120° to 170° C. Milly modified this process by using a smaller quantity of sulphuric acid (two to three and a half per cent.), which he allows to act at a temperature of 150° C. for two to three minutes only, and then boils with water. In this way the larger portion of the fat acids are white enough to be used for candle-making without previous distillation, while some twenty per cent. only of them needs to be distilled. The form of apparatus for the distillation of the free fatty acids produced in the sulphuric acid saponification is shown in Fig. 22. *T* is the superheater, from which steam at 300° C. is passed into the retort *D*, which is previously filled to three-fourths of its capacity with melted tallow through the supply-pipes *V V*. The fatty acids distil out of the tube *U*, are condensed by the worm *S*, and collected by the receiver *K*.

(4) *The superheated-steam process* of Wilson and Gwynne, before alluded to. This is at present carried out in both England and Germany. The apparatus devised by Mr. G. F. Wilson, of the Price Candle Company, of London, is shown in Fig. 23. The fat, previously heated in the flat vessel, *A*, by the waste-heat from the superheater below, flows into the retort *C*. This retort must be kept at from 290° to 315° C., and to this end is covered entirely above; the superheated steam at 315° C. comes

into the retort by the tube to the side, and some twenty-four to thirty-six hours is necessary to decompose and distil off a charge of fat. If the temperature falls below 310° C., the decomposition is extremely slow, while much above 315° C., acrolein forms from the decomposition of the glycerine. Before proceeding with the special processes of soap-making, stearine-

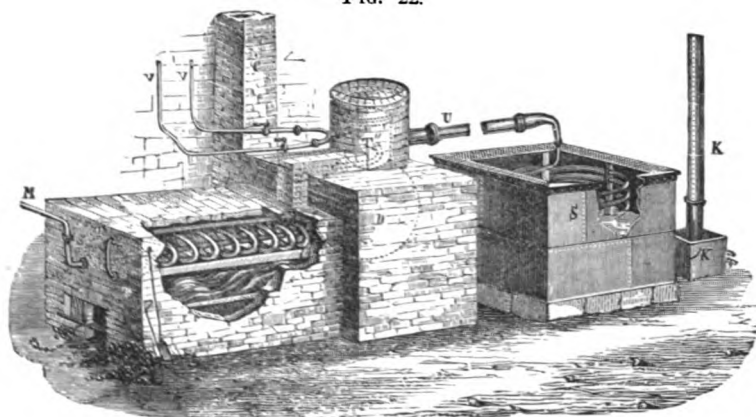
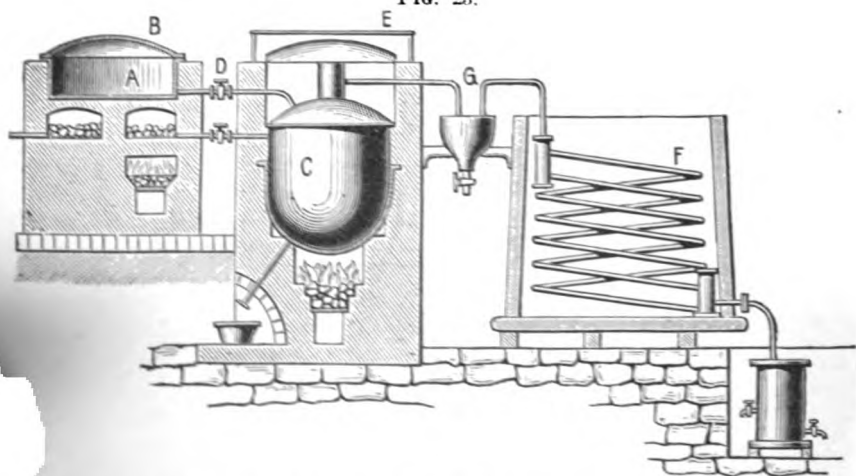
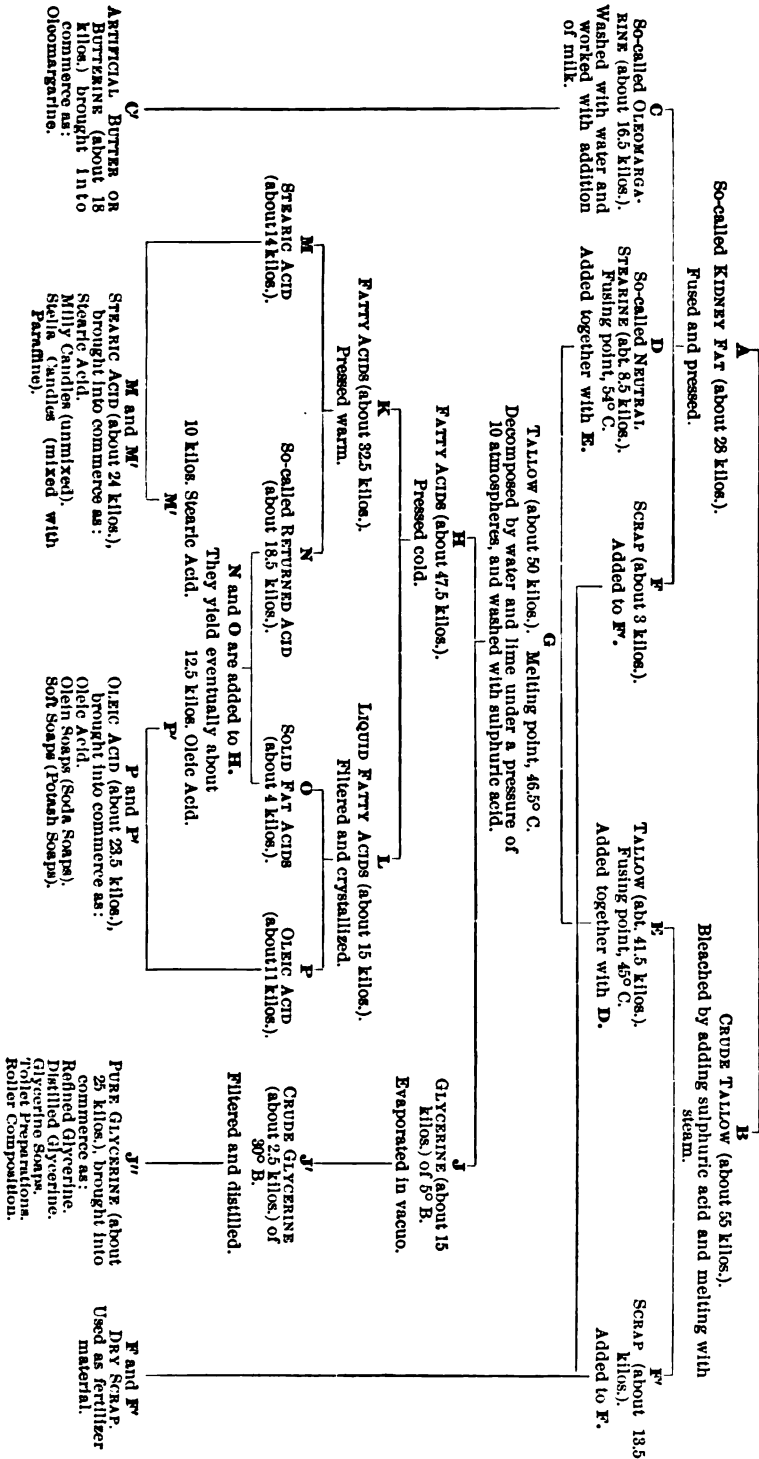
Fig. 22.

candle manufacture, oleomargarine and glycerine production, it will be well to present in schematic way the complete treatment of a fat such as tallow. The accompanying scheme is taken from Post's "Chemische Technologie," and shows the processes applicable and the products resulting from the technical utilization of tallow.

Fig. 23.

2. Practical Soap-making.—In the application of the first method of saponification of fats, that of the use of alkalies, we have, of course, always a potash or a soda salt of the fatty acid formed, which, singly or admixed, constitute the products known as soaps. A very great variety of soaps are known, the appearance and properties of which vary according to the method of manufacture. We may classify the several methods of manufacture as follows:

# PRACTICAL UTILIZATION OF A FAT.

(1) Boiling the fats in open vessels (coppers) with indefinite quantities of alkaline lyes until products of definite character are gotten. These are (*a*), soft soaps, in which the glycerine is retained, potash being the base; (*b*), the so-called "hydrated soaps," with soda for a base, in which the glycerine is retained, and of which "marine" soap may be taken as the type; (*c*), hard soaps, with soda for a base, in which the glycerine is eliminated, comprising three kinds,—curd, mottled, and yellow soaps.

(2) Acting upon the fats with the precise quantity of alkali necessary for saponification without the separation of any waste liquor, the glycerine being retained in the soap. This includes (*a*) soaps made by the "cold process," and (*b*) soap made under pressure.

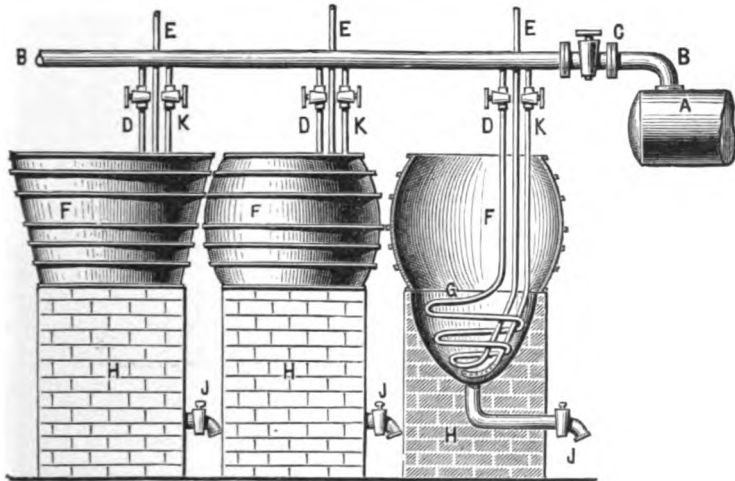
(3) Direct union of the fatty acids, as in "red oil" and caustic alkali, or alkaline carbonate.

The general outlines of these methods may be indicated:

In the manufacture of soft soaps the drying oils are preferably used. In England whale, seal, and linseed oil are chiefly used, in Continental Europe hemp-seed, linseed, rape-seed, poppy, and train oils, and in the United States cotton-seed oil and oleic acid. A potash lye containing some carbonate is used, and frequently a portion of the potash is replaced by soda. The soft soaps, after being boiled to the necessary degree, are not salted, so that the glycerine and any excess of alkali remains in the soap. For use in wool-scouring this excess of alkali is, however, unsuited, so that neutral soft soaps are specially sought to be obtained. The method of making "hydrated" or "filled" soaps is very similar to that of soft soaps. Fatty matter and soda lye are run into the copper, and the whole is boiled together, care being taken to avoid an excess of alkali at first; when saponification has taken place, lye is cautiously added until the soap tastes very faintly of alkali, when the soap is ready to be transferred to the frames, without any salting or separating of the mixture. Marine soap, for use with sea-water, is made in this way, and is entirely cocoa-nut oil soap. The well-known Eschweger soap is also made by this general method from a mixture of cocoa-nut oil and other fats, saponified either separately or together, and containing the glycerine and water in the soap mass.

The manufacture of true hard soaps, which still constitute the great bulk of those made in England and the United States, requires more time and care than the varieties just mentioned. Melted fat and a quantity of soda lye of about 11° B., equal to one-fourth that needed for complete saponification, are simultaneously run into the copper and steam turned on. The "soap-copper," as shown in Fig. 24, is an iron kettle, or series of kettles, set in masonry, and equipped with pipes for both open and closed steam, and provided with an outlet for the discharge of the waste lyes when required. They may be used in series, or extra large single ones used. Strong lye should not be used at this first stage, or saponification will not take place. When the mixture becomes homogeneous, lye of 20° to 25° B., in amount equal to that taken before, may be cautiously added. It is now boiled until a sample taken out has a firm consistence between the fingers. Common salt or a brine of 24° B. is now run in. A small sample removed on a spatula or trowel should now allow clear liquor to run from it. The boiling is then stopped, and the copper should be allowed to stand at least two to three hours. The contents now divide themselves into two portions, the upper consisting of soap-paste, containing water, and the lower consisting of "spent lye," holding in solution common salt and all the impurities of the

liquors, together with glycerine. It should contain no caustic soda and no soap. After removing the spent lye from below, the rest of the caustic soda lye is run in and the soap boiled up again. At this stage the rosin is usually added for rosin or yellow soaps. The boiling is now continued until the frothing mixture boils quietly and becomes clear, the process being known as "clear boiling." The copper is then boiled with open steam and a small quantity of lye of 12° B. allowed to run in until the soap separates in flakes and feels hard when cold, technically called "making the soap." Boiling is still continued for several hours to insure complete saponification, and it is then allowed to separate and harden. This procedure yields a curd

FIG. 24.

soap if no rosin has been added. If, after a soap is "made," the lye in which it is suspended is concentrated to a point short of that necessary to produce hard curd soap, and it is then transferred to the cooling frames with a certain quantity of lye entangled in it, these insoluble particles will, during the solidification of the soap, collect together and produce the appearance known as "mottling;" and the effect is heightened by the partial crystallization of the soap. The lye remaining in the cavities between the curds makes mottled soaps, the most suitable and really economical for washing clothes, etc., in hard waters, although not for toilet purposes. Mottling is sometimes added, as the peculiar greenish mottle, which becomes red on exposure, characteristic of Marseilles and Castile soaps, is produced by adding some solution of ferrous sulphate to the copper when the soap is nearly finished (about four ounces of the salt to one hundred pounds of the fat); the precipitated iron protoxide suspended in the soap is greenish, but it becomes peroxide in contact with air, to which the change to a red color on exposure is due. Yellow soaps are made from tallow and rosin, the proportion of rosin varying from one-sixth of the total fat to an equal weight, or even more, according to the quality of the soap desired. In the presence of the sodium oleate from the tallow, the rosin acids saponify readily and coalesce to form a very uniform soap.

In smooth or "cut" soaps water or thin lye is added to the contents of the copper before the soap separates finally to form the curd, and is taken

up in considerable amount, giving a smooth yet firm surface to the soap, instead of the hard, granular surface of the curd soap.

The so-called "cold process" requires the use of exact weights of well-refined fats and of caustic soda of a given specific gravity, the quantities being such that only just enough soda is present to completely saponify the fat. The materials are allowed to stand together for a short time and then thoroughly mixed in a copper provided with steam, agitating paddles, and kept at a temperature of not over 120° F. The reaction proceeds rapidly, and after some fifteen minutes the materials have so far united that they will not separate on standing, although the complete saponification of the materials may require days. They are then run out into the cooling-frames. It is obvious that soaps made in this way retain all the glycerine originally combined with the fatty acids disseminated through the particles of soap, and belong to the class known as "filled" or "padded" soaps, mentioned before. (See p. 62.)

When cocoa-nut oil alone is used, the temperature of working in this cold process need not be higher than 75° F. for summer and 90° F. in winter; if one-half tallow, 104° to 108° F.; and if two-thirds tallow, 113° to 120° F. is necessary.

Mixtures of cocoa-nut oil and other fats are frequently saponified in this way, the free acid of the cocoa-nut oil readily starting the process of saponification. A well-refined tallow can, however, be saponified in this way too, and mixtures of tallow and rosin worked up also into yellow filled soaps.

This combination of cocoa-nut oil with tallow and rosin can also take up in its saponification large quantities of water-glass and similar "filling" material, so that a very large yield of a smooth filled soap is obtained. Thus a mixture of one hundred kilos. of cocoa-nut oil, seventy-five to eighty kilos. of rosin, three hundred kilos. of water-glass, one hundred to one hundred and fifty kilos. of tallow, and two hundred and forty kilos. soda lye of 33° B., will make eight hundred kilos. of a finished soap.

Saponification under pressure has also been frequently tried, the object being to shorten the time required for open boiling. In this case the quantity of alkali used must be accurately adjusted to the fat to be saponified, the glycerine is retained in the ultimate product. The process is carried out in an autoclave or pressure-boiler, the temperature is allowed to rise to about 310° F. (154.4° C.), equivalent to a steam-pressure of sixty-three pounds to the square inch, and kept at this for an hour, when the contents are discharged into a cooling-frame.

There remains to be noted the process of soap-making, in which we start not with a fat, but with the free fatty acid, as in the "red oil" or crude oleic acid obtained in stearine candle manufacture. (See p. 67.) These oleine soaps, as they are called, are made preferably from the oleic acid resulting from the saponification of tallow or palm oil by the lime process. That obtained in the distillation process is not so well adapted for use here. The oleic acid may be saponified either with carbonate or with caustic alkali. The former process has the disadvantage that the escaping carbonic-acid gas causes a strong frothing which easily leads to boiling over. One hundred kilos. of the oleic acid obtained in the lime-saponification yield one hundred and fifty to one hundred and sixty kilos. of soap. The acid obtained by distillation always yields somewhat less. Frequently the oleic acid before saponifying is changed by nitrous acid into the isomeric elaidic acid, which is as hard as tallow, and from which a very fine soap can then be made resembling tallow

soap, and capable of being worked at will into a curd soap or a cut soap. If to be made with carbonate of soda, the copper is filled to one-third its capacity with the oleic acid and the calculated amount of half-crystallized and half-calcined soda added, little by little, while the heating and thorough agitation of the liquid is kept up. When the soap becomes thick and all foaming has ceased, the soap is filled at once into the forms to cool. The portion of crystallized soda used supplies all the water needed for the saponification.

In saponification with caustic alkali, a strong lye (25° B.) is taken. No emulsion forms, but a lumpy, mortar-like mass, which, however, as the alkali is more fully taken up and the lye becomes weaker, gradually goes over into ordinary soap-paste. The soap is separated by the addition of a strong lye instead of salting it.

After the finishing of the soap in the copper, it may either be put direct into the cooling frame, or it may be transferred to mixing tanks, where various solutions or substances are incorporated with it prior to its being allowed to solidify.

**Soap-frames** are of two kinds, according as it is desired to cool the soap slowly or quickly. When slow cooling is required, as is always the case with mottled soap, wooden frames, usually of pine, are employed. These are built up in horizontal sections, nine to twelve inches deep, each section lined with thin sheet-iron, as shown in Fig. 25. Most curd and all yellow soaps are cooled rapidly in cast-iron frames of any desired shape and size. Such an iron soap-frame is illustrated in Fig. 26. The sides and ends of the frame are easily removed after the thorough solidification of the soap, and the block is then left upon the truck, which served as the bottom of the frame. It is now ready for the cutting into slabs and bars. This is now almost universally done by machinery, and the truck containing the hardened block is run at once into the large frame containing the cutting wires. Such a frame, although of smaller size, and used for slabs of soaps only, is shown in Fig. 27. The best piano-forte wire is necessary for these cutting frames, as the tension is very great when the soap is pressed through the wires.

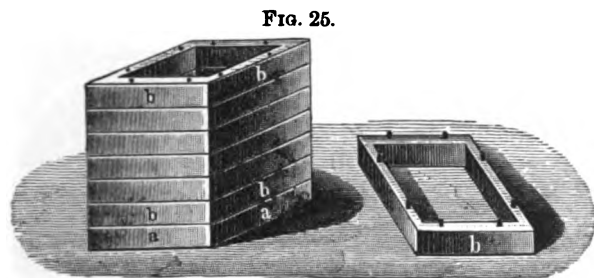
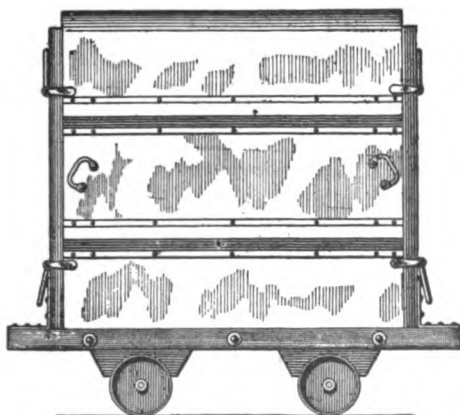



Fig. 25.

Fig. 26.

While the soaps thus far spoken of are adapted for general or laundry purposes, there is a distinct class of soaps known as *toilet soaps*. As these

are to be applied to the skin they must answer other requirements, the most important of which is that they shall not contain any free alkali. Some dermatologists even demand that there shall always be some unsaponified fat. We may distinguish transparent soaps, remelted soaps, and milled soaps.

Transparent soaps may be made either by the spirit process, in which case the stock soap is dissolved in alcohol, the solvent almost all distilled off, and the mixture then run into frames to gelatinize and solidify by gradual evaporation of the remaining alcohol, or the cold glycerine process. In this case the warm fatty materials employed (of which castor oil is generally a large ingredient on account of the readiness with which it saponifies) are intimately mixed with soda ley; soluble coloring matters and essential oils or other scenting material are then stirred in and the whole allowed to stand. The glycerine which forms on saponification tends to cause the soap to take a translucent appearance. Perfect transparency can be obtained by the addition of more glycerine, or what accomplishes the same result and is cheaper, cane-sugar. This latter ingredient, however, makes the soap irritating to sensitive skins.

In the remelting of soaps, followed chiefly in England, several stock soaps may be mixed together, coloring and scenting materials added, and the mass heated in a steam-jacketed pan. If the mixture is rapidly agitated, enough air-bubbles may be worked in to enable the cake of soap to float in water, even after compression in the stamping press, producing a toilet soap which "floats" on water. The addition of some pearlash (potassium carbonate) is also made at times to improve the lathering power of the soap, but such soaps are alkaline and injurious to delicate skins. The finest toilet soaps, however, are made by "milling," a process first carried out in France. The bars of stock soap are first "stripped," or cut into slices by a slicing machine. The chips are dried in a warm air-chamber until only a few per cent. of water remains, and then ground between heavy horizontal rollers of the milling machine. At this stage the various coloring and perfuming ingredients are added, or unguents like lanolin and vaseline. The thoroughly mixed material is then put into a cylindrical barrel, in which it is compressed by a piston and comes out as a continuous bar, which is cut into lengths and stamped into cakes. The advantages of this method are, first, that inasmuch as no artificial heat is applied, delicate flower perfumes, etc., can be readily incorporated with the soap mass which it would be impossible to use with a remelted soap, because the heat would dissipate or destroy the odoriferous matter; and, secondly, that as the resulting tablets usually contain only a small quantity of water, a given weight of soap-cake or tablet generally contains a much larger quantity of actual soap than another cake of the same weight prepared by remelting or by the cold process, whilst, being harder and stiffer, it lasts longer, wasting less rapidly during use. Spherical cakes and wash-balls are finished by turning and polishing in a kind of lathe. Sometimes the polishing is finished by the use of a cloth dipped in alcohol.

Shaving creams are made by the cold process from refined lard and caustic potash, adding cocoa-nut oil in small amount to facilitate the making of lather.

3. Stearic Acid and Candle Manufacture.—For the extraction of stearic acid, the washed fatty acids (see p. 59) are heated to the

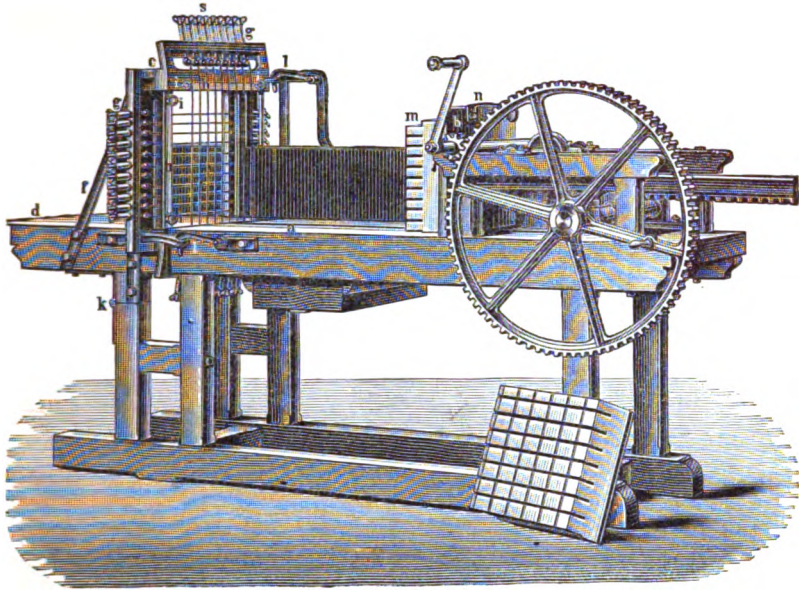
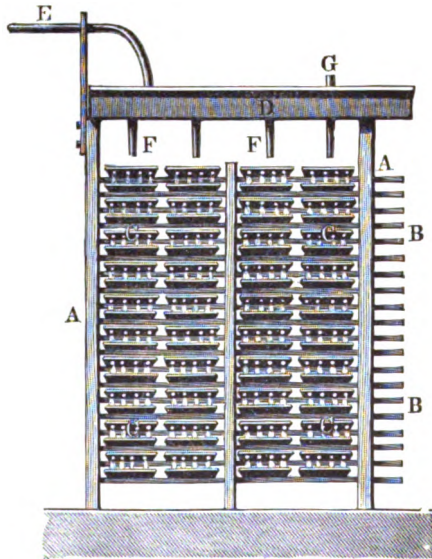
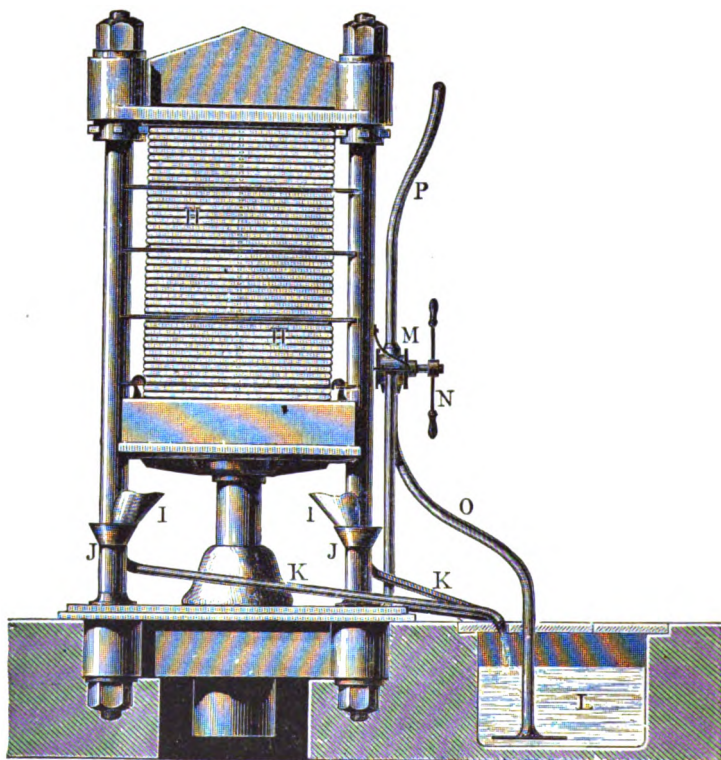
Fig. 27.

melting point and run into dishes or troughs made of tin, as shown in Fig. 28. These are placed in a room, the temperature of which is kept at 68° to 86° F. (20° to 30° C.), and left for two to three days, or until the contents have granulated, as the palmitic and stearic acids crystallize, when the dishes are emptied into canvas or woollen bags, which are carefully deposited between the plates of an upright hydraulic press, as shown in Fig. 29. Pressure is now exerted, increasing in degree until the flow of the liquid oleic acid ceases. The hard, thin cakes of crude stearic acid so obtained are then melted down again with steam, and after settling, the melted acid run into the tin dishes and placed aside to cool. The temperature of the cooling-room in this case should be higher than before, or about 86° F. (30° C.). The blocks of stearic acid gotten are ground to meal, filled in bags of hair or wool, and then submitted to a second pressure in a horizontal hydraulic press, the plates of which can be heated. In this press, a pressure of six tons per square inch, at temperatures of from 104° to 120° F. (40° to 49° C.), is reached. The cakes so obtained are melted by

Fig. 28.

steam, a little wax being sometimes added to destroy the crystalline structure of the stearic acid, which somewhat unfits it for candle-making.

The yield of stearic acid obtained varies according to the fat used and the process of saponification employed. F. A. Sarg's Sons (Vienna) use three per cent. of lime under a pressure of ten atmospheres, and get ninety-five per cent. of crude fat acids and thirty per cent. of glycerine water (5° to 6° B.), and a final yield of forty-five per cent. stearic acid, fifty per cent. of oleic acid, and five to six per cent. of glycerine. In England, with the sulphuric acid and distillation process, they get sixty to seventy or even seventy-five per cent. of fat acids suitable for candle-making, although inferior to that obtained in the lime process.

Fig. 29.

Palm oil is now used in enormous quantities for the production of palmitic acid at Price's Candle Company's works, as well as by almost every candle manufacturer in Great Britain, about twenty-five thousand tons being annually consumed. In many continental countries a prohibitive duty prevents its employment. From this palmitic acid the finest composite candles are made by hot-pressing the distilled palmitic acid.

Palmitic acid for candle-making is also made commercially, according to a process of St. Cyr-Radisson, by fusing oleic acid with a great excess of caustic potash, the products of the reaction being potassium palmitate, potassium acetate, and hydrogen. As carried out in Marseilles, the oleic acid and potash lye of 41° B. are put into an autoclave provided with a

mechanical agitator, and heated until steam ceases to be given off, when the open manhole is closed, and the heat continued until 554° F. (290° C.) is reached. Decomposition now commences, and much hydrogen is given off through an escape-tube set in the lid of the boiler. At 608° F. (320° C.) the odor of the evolved gas suddenly changes, and destructive distillation begins. This is arrested by blowing in steam at once, and the contents are run out. The potassium palmitate is then washed, decomposed with sulphuric acid, the free acid washed and distilled. The product of the distillation is white, and burns excellently when made into candles.

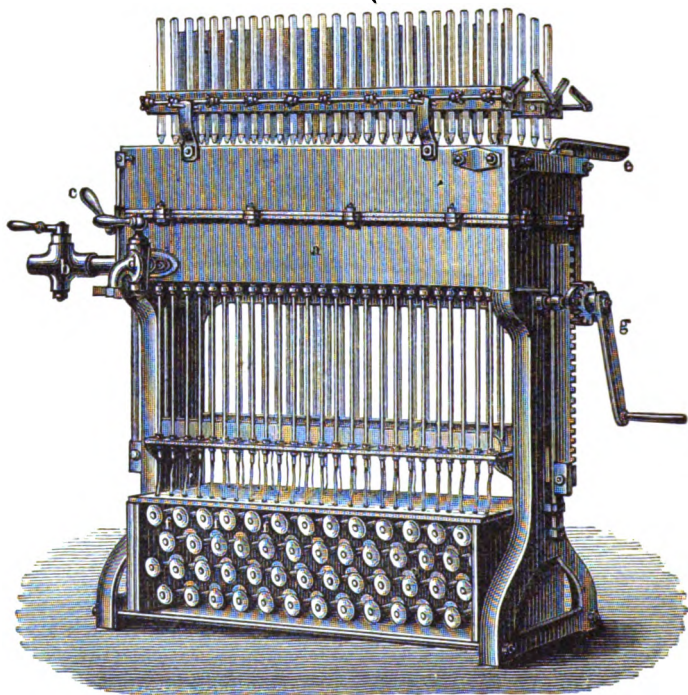
In the manufacture of candles, the first operation is the preparation of the wick. For dip-candles the wick is twisted, for others it is plaited, and the kind of plaiting must also vary according to the material used. Stearine candles require a moderately tightly-braided wick, paraffine candles an extra tight braid, and for spermaceti and wax, on the other hand, the braids are measurably loose. After being twisted, or plaited, the wicks are dried and then dipped into a pickling liquor, which is to retard combustion and help in the destruction of the ash. The pickle usually consists of a solution of boracic acid, ammonium phosphate, or ammonium chloride. Three plans of candle-making are at present in use,—dipping, moulding, and pouring. The first is employed for common tallow candles, which are accordingly called "dips." Under a frame holding the suspended wicks are placed troughs containing melted tallow, into which the wicks are repeatedly dipped. After each dipping the adherent fat is allowed to cool sufficiently to retain a fresh coating on immersion. When the candles have thus grown to the proper thickness they are left to cool and harden. These cheap "dips" are, however, now being replaced by small, moulded "composite" candles, as well as candles made from the softer, paraffine scale. Pouring is used only with wax candles, which cannot be moulded because of the adhering or cracking of the wax in removing it from the moulds. A well-made wax candle should show rings like a tree, where the different layers have been superposed. By far the greater number of candles are moulded, by which process they acquire a much more finished appearance. A form of frame in common use is represented in Fig. 30.

The materials in general use for candle-making are tallow, palmitic and stearic acids, paraffine, ozokerite or ceresine, spermaceti, and beeswax. Very generally, several of these materials are admixed. Stearic candles have a small quantity of paraffine added to obviate the crystalline structure of the stearic acid; paraffine candles always have five to ten per cent. of stearic acid in them, to prevent the softening and bending of the paraffine when warmed. Spermaceti and beeswax are more expensive than the other materials, and are only used now for special purposes, as for church-candles and carriage-lights. Ozokerite gives the paraffine candle of highest fusing point, being some six degrees higher than any other variety of paraffine. Colored paraffine candles are made by dissolving the coloring matter (vegetable or aniline dyes, not mineral colors) in stearic acid, and then mixing this with the paraffine, which itself does not take up the color. Paraffine and other transparent candles must be filled in the mould very hot, and after all air-bubbles have escaped, the moulds must be rapidly cooled by a large flush of cold water to prevent the paraffine, etc., from crystallizing and thus causing opacity,

Of interest in this connection is the table of illuminating equivalents, or quantities of different illuminating materials necessary to produce the same amount of light, prepared by Frankland.

| | | | |
|---|---|---|---|
| Young's paraffine oil | 1.00 gallons. | Sperm candles | 22.90 pounds. |
| American petroleum, No. 1 | 1.26 gallons. | Wax candles | 26.40 pounds. |
| American petroleum, No. 2 | 1.30 gallons. | Composite (stearine) | 29.50 pounds. |
| Paraffine candles | 18.60 pounds. | Tallow | 36.00 pounds. |

4. Oleomargarine, or Artificial Butter Manufacture.—The manufacture of a butter-substitute from the solution of palmitin in olein, which is known as oleomargarine, is a fat industry, but, because of its close relations to natural butter made from cows' milk, it will be

Fig. 30.

considered as supplementary to the description of butter under milk industries. (See p. 256.)

5. Glycerine Manufacture.—For many years after the development of the soap and candle industries, no attempt was made to recover the glycerine which was liberated in the saponification. Its applications in medicine and for technical purposes have made it important to extract and purify it, however, and it has now assumed almost equal importance with the other fat constituents. The two methods of saponification, by which glycerine has been obtained on a large scale, are the process of Wilson & Payne, of decomposing the fats by superheated steam and after distillation (see p. 59), and the lime autoclave process of Milly. (See p. 58.) In the distillation process, moreover, by suitable arrangement for fractional condensation, it is found possible to concentrate the aqueous glycerine in the process of distillation. Care must be taken that the temperature of 600° F. (315° C.) is not exceeded, and that plenty of steam is present, otherwise some glycerine is decomposed and acrolein is formed. In the Milly process, after

the decomposition of the fat is completed in the autoclave, the contents are blown out into a tank and the "sweet water" (glycerine) is run off. The concentrating may be done in contact with air or the apparatus may be worked in a Yaryan or similar evaporator. Evaporation is continued to 26° B. (1.220 specific gravity), when the glycerine is of a brownish color, and is known as "raw," in which state it is sold for many purposes, and contains about ninety per cent. of glycerine and traces only of mineral impurities. At Price's Candle Company's works the further purification is conducted as follows. The raw glycerine, specific gravity 1.240 to 1.245, is heated in a jacketed pan with that kind of animal charcoal known as ivory-black, and is then distilled; this alternate treatment is repeated as often as is necessary. The distillation is performed with superheated steam in a copper still provided with copper fractional condensers, the still being also heated externally; the operation is performed at as low a temperature as is consistent with distillation, usually about 440° F. (227° C.).

It is obvious that in soap-making, as enormous quantities of the fats are decomposed, corresponding quantities of glycerine go into the spent lyes. It is only very recently that it has been attempted to recover this glycerine, and no perfectly satisfactory process seems, as yet, to have been adopted. More practical, in the opinion of those qualified to judge, seems to be the idea recently put forward to deglycerinize all fats before saponifying them. The process of Michaud Frères, of Paris, as carried out by the Continental Glycerine Company, of New York, realizes this idea very successfully.

According to their patent "the fatty matter is subjected in a close vessel to the action of the steam, at a pressure of one hundred to one hundred and thirty pounds per square inch, and at corresponding temperature in presence of one-fourth to one-third part its weight of water and one-fifth to three-fifths per cent. of its weight of the oxide of zinc, known commercially as zinc white, or a like proportion of zinc powder or zinc gray, which is a residue in the treatment of zinc, being a mixture of zinc with its oxide. . . . The very small proportion of mineral substance used is sufficient for dispensing with the acid treatment applied for decomposing lime soap, and the product obtained, consisting almost exclusively of acid fat, can be converted by the acids usually employed into soap or candles. In soap-making, the dissolving powers of the caustic alkalies remove all objections to the presence of the zinc if it should be used in excess. The reducing power of the zinc powder prevents discoloration of the acid fats such as results from the ordinary treatment." The glycerine thus produced finds a ready sale, as it runs from the evaporators, and from it, as "crude," ninety-six per cent. of pure glycerine can be obtained.

5*a*. Nitro-Glycerine and Dynamite.—In 1847 Sobrero discovered a very interesting derivative of glycerine, and in 1862 A. Nobel gave it to the world as a technical product of the greatest importance. When strong glycerine is gradually added to a well-cooled mixture of very strong nitric and sulphuric acids, it is converted into glyceryl nitrate, or nitro-glycerine. For the manufacture of nitro-glycerine on a large scale, Nobel recommends that one part of good glycerine be allowed to flow in a thin stream into a well-cooled mixture of four parts of concentrated sulphuric acid and one part of the very strongest nitric acid (1.52 specific gravity), the mixture being contained in a wooden vessel lined with lead. Means should be provided by which the mixture can at once be run into a large quantity of water should the action threaten to become too violent. On standing, the nitro-glycerine sepa-

rates as a layer on the surface of the acid, and is skimmed off and washed with water and solution of sodium carbonate to get rid of every trace of free acid. Or, according to the same authority, a mixture is made of one part nitre with 3.5 parts of sulphuric acid (1.83 specific gravity), the mixture cooled to 32° F. (0° C.), and the liquid poured off from the acid potassium sulphate, which separates out; into this liquid the glycerine is slowly dropped, the mixture poured into water, and the separated nitro-glycerine washed thoroughly and dried. The yield is two hundred and twenty-three per cent. of the glycerine used.

It has been suggested to mix the glycerine beforehand with the sulphuric acid, and then run this mixture into the nitric acid, and it is claimed that the elevation of temperature is less than when the ordinary method is followed; but the process does not seem to have been satisfactory in practice when tried in England.

When absorbed by infusorial earth, "kieselguhr," sawdust, mica powder, or other inert porous material, nitro-glycerine forms the different varieties of dynamite, and, when combined with gun-cotton, it constitutes the explosive known as "blasting gelatine."

## III. Products.

1. PURIFIED OILS, FATS, AND WAXES, AND PRODUCTS FROM THE SAME. —Most of the important oils, fats, and waxes have already been described as raw materials, and the methods of purifying them have been noted. The purified oils are in some cases the final products sought, and, in some cases, only improved raw materials for the main industries, like soap-making, candle-making, and glycerine extraction. These purified oils having, therefore, been referred to as raw materials, will not be further noted. A number of side-products, obtained with or produced from these oils, remain to be mentioned.

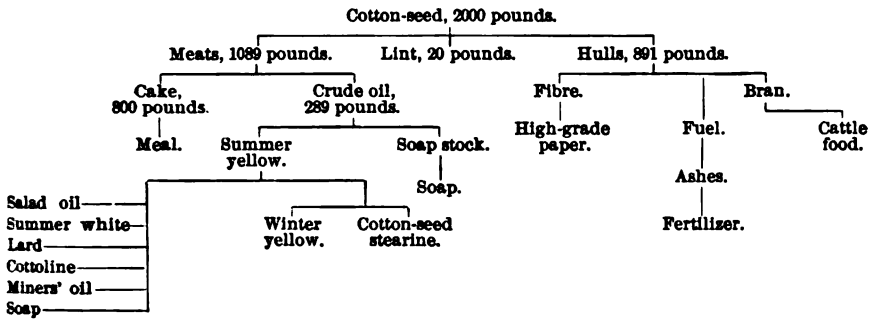
One of these minor products of great value is the oil-cake, or compacted mass of crushed seeds or nuts, from which the oil has been expressed or extracted. This contains all of the woody fibre and mineral matter of the seed or nut, the residue of oil or fatty matter not extracted, and, what gives it special value, the proteids or nitrogenous constituents. The oil-cake thus becomes a most valuable cattle food and a basis for artificial fertilizers. The following table gives the composition of a number of the most important oil-cakes:

| | Water. | Fat. | Non-Nitrogenous Materials. Woody Fibre. | Ash. | Protein Material. | Nitrogen. Per Cent. |
|---|---|---|---|---|---|---|
| Earth-nut cake | 11.50 | 8.80 | 31.10 | 7.25 | 41.35 | 6.80 |
| Cotton-seed cake | 13.00 | 7.50 | 51.00 | 8.50 | 20.00 | 2.90 |
| Rape-oil cake | 10.12 | 9.23 | 41.93 | 6.48 | 31.88 | 5.00 |
| Colza-oil cake | 11.35 | 9.00 | 42.82 | 6.28 | 30.55 | 4.50 |
| Sesame-oil cake | 10.35 | 10.10 | 38.80 | 9.80 | 31.93 | 5.00 |
| Beech-nut cake | 11.40 | 8.50 | 49.80 | 5.30 | 24.00 | 3.20 |
| Linseed cake | 10.56 | 9.83 | 44.61 | 6.50 | 28.50 | 4.25 |
| Camelina cake | 9.60 | 9.20 | 50.90 | 7.00 | 23.30 | 3.60 |
| Poppy-oil cake | 9.50 | 8.90 | 37.67 | 11.43 | 32.50 | 5.00 |
| Sunflower-oil cake | 10.20 | 8.50 | 48.90 | 11.40 | 21.00 | 2.40 |
| Hempseed cake | 10.00 | 8.26 | 48.00 | 12.24 | 21.50 | 3.30 |
| Palm-nut cake | 9.50 | 8.43 | 40.95 | 10.62 | 30.40 | 4.50 |
| Cocoa-nut cake | 10.00 | 9.20 | 40.50 | 10.50 | 30.00 | 4.50 |

It will be seen in this table that they vary in proteids or flesh-forming constituents quite widely. All of these cakes, however, are too rich in these proteids and in fats to be used unmixed as fodder. They are, in practice, mixed with cereals, hay, and straw, and then constitute a valuable food. The ash is, moreover, very rich in phosphoric acid and in potash, and this explains its value for fertilizer manufacture.

Thus it is stated that, as a fertilizer, one ton of cotton-seed-hull ashes has as much value as four and one-half of average hard-wood ashes, or fifteen of leached hard-wood ashes.

The amount of oil-cake obtained from the expression of the different vegetable oils is enormous. Thus it is stated that one ton of hulled cotton-seed (constituting forty per cent. of the raw cotton) will yield eight hundred pounds of cotton-seed cake and forty-five gallons of crude cotton-seed oil. The amount of crude cotton-seed annually obtained in the United States is estimated at four thousand million pounds, half of which only is required for sowing.

The accompanying table, prepared by Grimshaw, will show how thoroughly the cotton-seed is now utilized:

An important manufactured oil is what is known as "Turkey-red oil," used in the process of alizarin dyeing. (See p. 487.) There are, in fact, two entirely distinct oils known under this name. One is simply an inferior grade of olive oil, that known as "Gallipoli oil," and for this particular use is prepared from somewhat unripe olives, which are steeped for some time in boiling water before being pressed. This treatment causes the oil to contain a large proportion of extractive matter, and hence it soon becomes rancid. This preparation has long been used in the old process of Turkey-red dyeing, under the name *huile tournante*. The other, used for producing alizarin reds by the quick process, is the ammonium salt of *sulpho-ricinoleic acid* ($C_{18}H_{33}(HSO_3)O_3$), a body which is obtained mixed with unaltered glycerides and with products of its decomposition by the action of sulphuric acid upon castor oil.

From linseed oil, as the most important of the class of drying oils, is prepared a product of great value for paint and varnish manufacture. (See p. 101.) What is called "boiled oil" is linseed oil, which has been heated to a high temperature (130° C. and upward), while a current of air is passed through or over the oil, and the temperature increased until the oil begins to effervesce from evolution of products of decomposition. By adding litharge, red-lead, ferric oxide, or manganese dioxide, or hydrate, during the process

of boiling, the oxidation and consequent drying of the product are still further facilitated. The nature, proportion, and mode of adding these substances are usually kept jealously secret. Lead acetate and manganous borate are among the most approved. The action of some, at least, of these "dryers" (*e.g.*, compounds of manganese) seems to be that of carriers of oxygen, while litharge dissolves in the oil and acts partly as a carrier of oxygen and partly as the base of certain salts which oxidize very rapidly.

Many of the fatty oils and notably some of the non-drying oils are capable of being thickened and increased, especially in specific gravity and viscosity, by having a stream of air blown through them. The products of this treatment are known as *blown oils* or *oxidized oils*. They are not resinified as when the drying oils are boiled with driers, but become thick and viscid like castor oil. This property is taken advantage of, therefore, in the production of heavy viscid products, which are used in admixture with mineral oils for the purpose of preparing lubricants for heavy machinery. While cotton-seed, rape, olive, earth-nut, lard, and linseed oils have all been utilized in this way, the two most commonly employed are rape and cotton-seed oils.

In carrying out the blowing operation, the oil is usually heated to 70° C. (138° F.) or slightly more, and air is then blown in through a vertical pipe which passes down nearly to the bottom of the kettle, the air being itself heated to the same temperature. In a short time the oil begins to oxidize and the temperature to rise. The steam is then shut off from the heating coils, and care must now be taken that the temperature does not rise above 80° C. (176° F.). The process usually lasts from twelve to forty-eight hours, according to the nature of the oil being treated and the character of the product desired. By continuing the operation, products may be obtained of specific gravity as high as from .985 to .999 even.

Blown oils vary in color from a clear yellow to a dark reddish yellow, and have a peculiar and somewhat disagreeable odor. They are very viscous, as dense or denser than castor oil, from which they differ in not being readily soluble in alcohol but in being soluble in petroleum spirit. Their perfect miscibility with heavy mineral oils is, however, their chief advantage. The percentage of free fatty acids is usually increased by the blowing operation and the percentage of insoluble fatty acids decreased, owing to the formation of soluble oxyacids.

The following table from Lewkowitsch ("Oils, Fats, and Waxes," 2d ed., p. 734) will show the change undergone by rape oil in consequence of the blowing operation :

| | Specific gravity at 15.5° C. | Free acid as oleic. | Saponification value. | Iodine value. | Insoluble acids. | Soluble acids. |
|---|---|---|---|---|---|---|
| Rape oil . . . . . . . . | 0.9141 | 5.10 | 173.9 | 100.5 | 94.76 | 0.52 |
| Same, 5 hours' blowing . | 0.9275 | 5.01 | 183 | 88.4 | . . | |
| Same, 20 hours' blowing | 0.9615 | 7.09 | 194.9 | 63.2 | 85.94 | 10.02 |

2. SOAPS.—In noting the processes for practical soap-making, the following classes of soaps were indicated : (1) compact soaps, including (*a*) curd [illegible]s, (*b*) mottled soaps, and (*c*) yellow soaps ; (2) smooth or cut soaps ; (3) [illegible] or padded soaps ; and (4) soft or potash soaps.

The most important difference between the compact, cut, and filled soaps is the amount of water present in the soap. In the compact soap it may vary from ten to twenty-five per cent., in the cut soap from twenty-five to forty-five per cent., and in the filled soap from forty-five to seventy-five per cent. In addition, the filled soap contains the glycerine, spent lye, and other impurities of the soap copper.

The following table of analysis, by Mr. C. Hope, as quoted by Allen,* will illustrate the composition of a variety of soaps belonging to these several classes :

| NAME OF SOAP. | MATERIALS. | Fatty and resin anhydrides. | Soda existing as soap. | Silica. | Soda as silicate. | Sodium carbonate and hydrate. | Neutral salts, lime, and iron oxide. | Water. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| White, No. 1 . . . . . . . . . | Tallow . . . . . . . . . . . . | 69.06 | 8.98 | .01 | . . | .27 | .72 | 21.14 | 100.18 |
| White, No. 2 . . . . . . . . . | Tallow and cocoa-nut oil . . | 60.50 | 6.82 | .06 | . . | .06 | .39 | 32.20 | 100.03 |
| White, No. 3 . . . . . . . . . | Tallow and cocoa-nut oil . . | 55.71 | 6.90 | .03 | . . | .92 | .26 | 36.54 | 100.36 |
| White, No. 4 . . . . . . . | Tallow and cocoa-nut oil . . | 44.27 | 6.23 | 7.02 | 2.36 | .75 | 1.00 | 38.14 | 99.77 |
| Cold water, No. 1. . . . . . | Tallow, rosin, and cotton-seed oil . . . . . . . . . | 71.30 | 7.98 | 1.07 | .48 | .75 | .82 | 17.44 | 99.84 |
| Cold water, No. 2. . . . . . | Tallow, rosin, and cotton-seed oil. . . . . . . . . . | 49.95 | 7.00 | 2.34 | 1.01 | .33 | 1.01 | 38.18 | 99.82 |
| Olive oil, No. 1 . . . . . . . . | Olive oil . . . . . . . . . . | 71.20 | 7.58 | .06 | .03 | .22 | 1.03 | 19.70 | 99.82 |
| Marseilles, No. 1 . . . . . . . | Chiefly olive oil . . . . . . | 62.66 | 7.27 | .06 | .03 | .77 | 1.22 | 28.20 | 100.21 |
| Palm oil, No. 1 . . . . . . | Palm oil . . . . . . . . . . | 59.28 | 6.65 | .42 | .01 | .39 | .76 | 32.35 | 99.86 |
| Mottled . . . . . . . . . . | Palm-nut oil . . . . . . . . | 38.89 | 5.76 | 6.40 | 1.29 | 1.62 | 2.53 | 38.70 | 95.19 |
| Satinet . . . . . . . . . . . | Tallow and rosin . . . . . . | 59.92 | 6.76 | .02 | . . | .92 | 1.70 | 31.30 | 99.75 |
| Glasgow almond . . . . . . | Tallow and rosin . . . . . . | 42.41 | 4.14 | 5.64 | 1.59 | 2.76 | .51 | 42.88 | 99.93 |
| Pale Rosin, No. 1 . . . . . | Tallow and rosin . . . . . | 60.69 | 7.22 | .04 | . . | .10 | .60 | 31.22 | 100.00 |
| Pale Rosin, No. 2 . . . . . | Tallow and rosin . . . . . . | 48.20 | 5.00 | .42 | .18 | .15 | .90 | 45.00 | 99.80 |
| Pale Rosin, No. 3 . . . . . | Tallow and rosin . . . . . . | 39.92 | 4.70 | .62 | .25 | .20 | 1.81 | 52.40 | 99.90 |
| Milling . . . . . . . . . . | Not mentioned . . . . . . . | 63.06 | 7.25 | .02 | . . | .10 | 1.90 | 27.47 | 100.00 |
| Yellow (for foreign markets) | Not mentioned . . . . . . . | 10.90 | 1.36 | .03 | . . | Trace | 3.27 | 84.00 | 99.56 |
| Marine (for emigrants) . . | Palm-nut oil . . . . . . . . | 19.42 | 3.11 | 9.00 | 3.98 | 3.00 | 5.64 | 53.32 | 97.47 |

Two of these samples, those designated as "mottled" and "marine," were prepared by the "cold process" (see p. 64), which accounts for the totals being appreciably less than 100.00, as the glycerine was retained in the soap.

The chief soaps of pharmacy, as analyzed by M. Dechan,† are composed as follows :

| DESCRIPTION OF SOAP. | Fatty acids. | Combined alkali. | Free alkali. | Silica. | Sulphates and chlorides. | Insoluble matter. | Water. | Insoluble in alcohol. |
|---|---|---|---|---|---|---|---|---|
| Hard soap (*sapo durus*) . . . | 81.5 | 9.92 | .08 | .00 | .28 | 0.20 | 10.65 | 0.50 |
| White Castile soap (*s. Cast. alb.*) | 76.7 | 9.14 | .09 | .00 | .36 | 0.90 | 13.25 | 0.60 |
| Mottled Castile soap . . . . | 68.1 | 8.9 | .19 | .15 | .63 | 0.80 | 21.70 | 1.30 |
| Tallow soap (*sapo animalis*) . | 78.3 | 9.57 | .28 | .00 | .47 | 0.40 | 12.50 | 1.10 |
| Soft soap (*sapo mollis*) . . . | 48.5 | 12.6 | .38 | .17 | .93 | 1.00 | 39.50 | 1.60 |

* Allen, Commercial Organic Analysis, 2d ed., vol. ii. p. 272.
† Pharmaceutical Journal [3], xv. p. 870.

Toilet soaps do not differ in essential composition from the best of compact and cut soaps, as given above, but they are perfumed and given small additions of cosmetic or hygienic preparations. They are prepared in one of three ways: (1), by a melting of plain soaps; (2), a cold perfuming and pressing of finely-divided plain soaps; and (3), direct preparation from the raw soap-making materials.

Transparent soaps are obtained by dissolving the soaps in alcohol and drying the solution in moulds,—a slow process.

Glycerine soaps are obtained by dissolving the soaps in glycerine by the aid of heat. The glycerine imparts a strength to the lather.

3. CANDLES.—The candle-making materials have already been enumerated. (See p. 69.) Tallow and wax candles were the earliest in use. Stearine candles, known also under the name of Milly candles, from the French inventor of several of the processes of saponification, came into use in 1831. About the same time paraffine, first obtained in quantity from bituminous shales, and later from ozokerite and petroleum, was used for candle-making. These are also known under the name of "Belmontin candles," from the locality of the J. C. & J. Field candle-works, in London. Candles of mixed stearic acid and paraffine, under the name of Stella or Apollo candles, were then manufactured. The Galician ozokerite is also purified by sulphuric acid, and under the name of ceresine (see p. 31) is used in Austria for candle manufacture. Beeswax and spermaceti, as before stated, are high-priced materials, and are used for special classes of candles. The paraffine and stearine candles and those which are mixtures of these materials are now most generally in use.

4. OLEOMARGARINE OR BUTTERINE. (See p. 256.)

5. GLYCERINE AND NITRO-GLYCERINE.—The chemical compound which is liberated along with the fatty acids when the fats are saponified by any of the various processes already narrated is a triatomic alcohol, called glycerine. When purified and made absolute, it is a colorless, viscid liquid, without odor, but with a pronounced sweet taste. The specific gravity of the absolute glycerine is about 1.266 at 15° C. When kept for a long time at 0° C., rhombic crystals are formed, their production being greatly facilitated by the presence of a ready-formed crystal. The crystals are hard and gritty, but deliquescent. It boils under ordinary pressure at 290° C., not without decomposition. It is highly hygroscopic, and is miscible with water in all proportions. Glycerine is miscible with alcohol in all proportions, but is insoluble in chloroform, benzene, petroleum spirit, carbon disulphide, or fixed oils. Glycerine is nearly insoluble in ether, from which it separates any alcohol or water. When glycerine is heated with a dehydrating agent (*e.g.*, concentrated sulphuric acid), irritating fumes of acrolein (acrylic aldehyde), $C_3H_3OH$, are evolved, smelling of burning fat. By far the largest application of glycerine is for the manufacture of nitro-glycerine, but it is also employed extensively in the manufacture of toilet soaps, for filling gas-meters and tubes in situations liable to be exposed to great cold, and in pharmacy and medicine. It is also used for the preservation of food products, and for the treatment (scheelizing) of wine, vinegar, and beer.

Nitro-glycerine is a heavy, oily liquid of 1.600 specific gravity at 15° C. The commercial preparation is usually yellowish to brownish, although the pure oil is colorless. It has no marked odor, but is sensibly volatile at ordinary temperatures, and the vapor causes a violent headache in those

unaccustomed to it; but people constantly employed in mixing and handling dynamite do not suffer from the effects. Nitro-glycerine has recently been employed in medicine, especially for the treatment of *angina pectoris.* Nitro-glycerine is not readily inflammable, and when ignited commonly burns with a greenish flame, without explosion. The most characteristic property of nitro-glycerine, and that which gives it by far its most important application, is that of exploding with extreme violence when smartly struck or compressed or when dropped on an iron plate heated to 257° C. The presence of free acid in nitro-glycerine, however, makes it liable to spontaneous decomposition and explosion.

Nitro-glycerine is easily saponified by alcoholic potash, and is reduced by various deoxidizing agents.

Nitro-glycerine in undiluted state is only exceptionally used now for explosive purposes, as in "torpedoing" oil-wells. For blasting purposes it is mechanically mixed or absorbed in some finely divided solid material.

Thus, *Dynamite No. 1* contains seventy-five per cent. of nitro-glycerine mixed with twenty-five per cent. of infusorial earth or kieselguhr. This mixture is then packed in cartridges of paraffined paper, constituting the "stick" of dynamite.

*Mica powder* consists of fine mica scales in which about fifty per cent. of nitro-glycerine is absorbed.

Next in order come explosives in which with the nitro-glycerine is combined an active base, either a nitrate or a mixture of nitrate and combustible substance, like charcoal or sulphur. The best known are:

*Dynamite No. 2* contains forty per cent. of nitro-glycerine, sodium nitrate thirty-eight, sulphur six, resin eight, and kieselguhr eight.

*Dynamite No. 3* contains nitro-glycerine fifteen, and eighty-five of a mixture of sodium nitrate, coal, and sodium carbonate.

*Vulcan powder* contains nitro-glycerine thirty, sodium nitrate fifty-two and five-tenths, and sulphur and charcoal seventeen and five-tenths.

*Atlas powder* A and B contains respectively seventy-five and fifty of nitro-glycerine, with sodium nitrate, wood fibre, and magnesium carbonate.

*Hercules powder* is similar to Atlas powder B, but contains only forty per cent. of nitro-glycerine and forty-five of sodium nitrate.

*Vigorite* contains, with thirty of nitro-glycerine, potassium chlorate forty-nine, potassium nitrate seven, wood pulp nine, magnesium carbonate and moisture five.

*Forcite* contains nitro-glycerine seventy-five, potassium nitrate eighteen, and gelatinized cotton seven. This latter ingredient is made by treating finely pulped cotton with steam under pressure until converted into a jelly, which is then mixed with the nitro-glycerine and the finely powdered nitrate added. The resulting product is a plastic mass resembling rubber, impervious to water, and relatively safe to handle.

Still another and more recently developed class of explosives are those in which nitro-cellulose or gun-cotton is combined with nitro-glycerine. The most important are:

*Blasting gelatine* or *gelatine dynamite*, which is a mixture of about eighty parts of nitro-glycerine with twenty of nitro-cellulose. Any unnitrated cotton or trinitro-cellulose interferes with the solution of the nitro-glycerine. The addition of four per cent. of camphor renders the mixture incapable of exploding when struck by a rifle bullet, but it can be detonated by a strong dynamite cap.

*Cordite*, which has been adopted by the English government as a standard "smokeless powder," contains nitro-glycerine fifty-eight, gun-cotton thirty-seven, and vaseline five. The nitro-glycerine and gun-cotton are first mixed, 19.2 parts of acetone added, and the pasty mass kneaded for several hours. The vaseline is then added and the mixture again kneaded. The paste is then forced through fine openings to form threads, which are dried at about 40° C. until the acetone evaporates. The threads are then cut into short lengths for use. They resemble a brown twine.

There are analogous explosives known as "smokeless powders" in which no nitro-glycerine at all enters, but which are merely cellulose nitrates or gun-cotton gelatinized and dried, as just described.

Picrates and picric acid are sometimes used; but, while powerful explosives, they are considered too unstable. *Melinite* and *Lyddite* are of this class.

## IV. Analytical Tests and Methods.

1. For Oils and Fats.—The total amount of oil in any particular oil-seed or other material is always an important matter to determine. This is best effected by treating the finely divided and previously dried substance with solvents under such conditions as to insure complete extraction. A form of apparatus in which this can be effected with the minimum amount of the solvent is what is called an *oleometer*. One of the best of these is the Soxhlet extractor, shown in Fig. 31, where *A* represents the extractor, *B* the distillation flask, *C* the condenser, and *D* the siphon-tube which empties the extractor. *A* is filled to three-fourths its capacity with the powdered oil-seed, and the bulb *B* is half filled with petroleum-ether, carbon disulphide, or proper solvent. The apparatus is then connected, as shown in the cut. As the Soxhlet apparatus is rather fragile and liable to break in handling, it may be replaced by simpler forms of extractors. Such an one is the Thorn extractor, shown in Fig. 32, the parts of which are easily understood from the illustration.

To recover the oil from its solution in the ether or other liquid employed, the solvent should be distilled off at a steam heat, and the last traces of it removed by placing the flask on its side and heating it in the water-oven until constant in weight.

The physical constants which are relied upon as characteristic in the case of oils and fats are specific gravity, and in the case of solid fats, fusing points. Boiling-points are not relied upon, because of the partial decomposition which fixed oils usually undergo when heated to high temperatures.

Specific gravity in the case of the liquid oils may be determined with the aid of the specific gravity bottle, the Sprengel tube, or the Westphal hydrostatic balance. The first of these is so well known from elementary works on chemistry as to need no description here. The Sprengel tube is a U-shaped tube, of which the two ends terminate in capillary tubes bent at right angles to the sides. The tube is completely filled with oil by immersing the open end of one tube in the liquid and gently sucking the air out from the other orifice. The U-tube is then placed in the mouth of a conical flask, containing boiling water (if the determination is to be made at 100° C.) or water at any other fixed lower temperature. The excess of oil that escapes at the orifices of the tube is wiped off with soft paper, and when the expansion ceases the tube is removed, wiped dry, allowed to cool, and weighed. The calculation can then be made, knowing the weight of the

tube empty and filled with water at the same temperature, or at 15° C. The Westphal balance is shown in Fig. 33. The thermometer or other plummet used displaces a definite volume of the oil, so that the loss in weight is the weight of this bulk of the oil under examination.

The melting-point of solid fats may be gotten with considerable accuracy by the melting-point method in general use in chemical laboratories. A

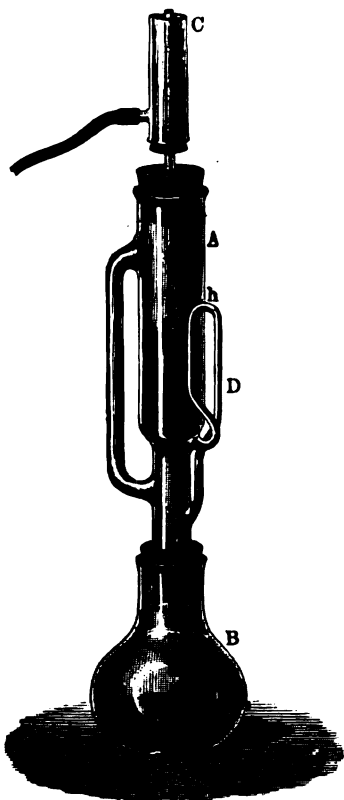
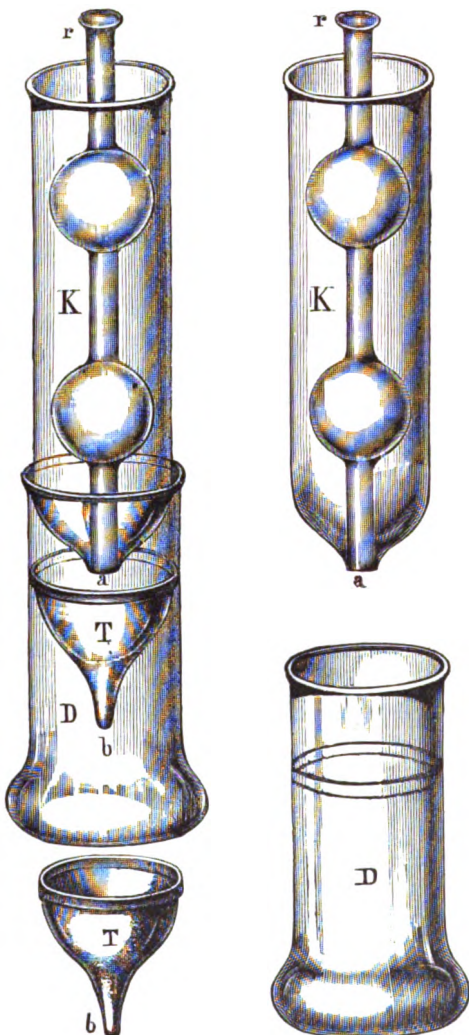
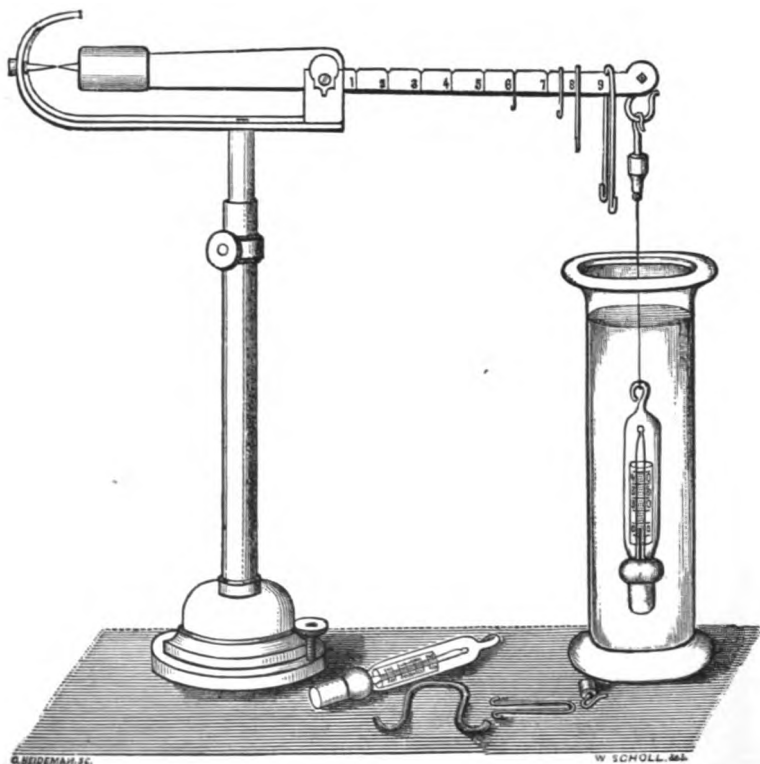



FIG. 31. FIG. 32.

capillary tube is filled with the fat while it is in the melted state, and then, after allowing it to cool and solidify, attach the tube to the stem of a delicate thermometer and immerse the thermometer in a beaker of water, which is then gradually heated until the melting-point of the fat is reached, and it liquefies in the capillary tube. The temperature at which this takes place is at once read off on the attached thermometer. To insure accuracy it is desirable to immerse the beaker of water in an outer vessel also filled with water, to which the heat is applied.

Of great importance with some of the fatty oils, such as sperm, rape, and lard oils, is the question of viscosity, and in quite a number the question of

cold test. The methods of determining these have been given in detail under mineral oils. (See p. 39.)

In some special cases the use of the oleo-refractometer, an instrument for noting the difference in refractive indices of oils, has proven valuable. Thus, true butter fat can be distinguished by this means from butterine or oleomargarine.

Fig. 33.

A number of chemical reactions have been taken at one time or another for the purpose of distinguishing between the different animal and vegetable ... and fats. Many are unreliable and the results contradictory, because ...dent upon special conditions, so that no great value attaches to them. ...tatement may fairly be said to apply to most of the color-reactions ... are gotten by the action of sulphuric and nitric acids upon the dif... oils and to the differences in elevation of temperature caused by the ...tion of concentrated sulphuric acid to the fatty oils.

Of much greater value, as affording general reactions for the distinguish...ng of the different oils and fats, are two processes of treatment now very generally adopted by chemists in the analysis of fats and fatty oils,—viz., the *saponification value* and the *bromine or iodine absorption value.*

...e saponification value (known also as Köttstorfer value) indicates the ...f milligrammes of potassium hydrate required for the complete ...n of one gramme of the fat or wax. The determination is ...s follows. About 1.5 to 2.5 grammes of the fat are treated with

twenty-five cubic centimetres of one-half normal alcoholic potash; when saponification has taken place, one cubic centimetre of an alcoholic solution of phenol-phthalein is added and the liquid titrated with one-half normal hydrochloric acid. A blank experiment is then made by titrating twenty-five cubic centimetres of the alcoholic potash alone, and the difference in the volumes of the acid used gives the volume of the potash solution neutralized by the fat, which is then calculated to milligrammes of potash for one gramme of fat used. The following are a few examples:

| OIL OR FAT. | Milligrammes of KOH per one gramme of fat. | Average saturation-equivalent. |
|---|---|---|
| Tallow | 193.2 to 198.0 | 286.9 |
| Lard | 192.0 to 196.5 | 288.8 |
| Cocoa-nut oil | 246.2 to 268.4 | 218.4 |
| Palm-nut oil | 220.0 to 247.6 | 240.8 |
| Olive oil | 191.0 (average) | 293.7 |
| Cotton-seed oil | 193.8 (average) | 289.4 |
| Rape oil | 173.3 (average) | 323 7 |
| Linseed oil | 191.3 (average) | 293.2 |
| Butter fat | 221.5 to 232.4 | 247.0 |
| Butterine | 193.5 to 196.5 | 287.7 |
| Sperm oil | 123.4 to 147.4 | 380 to 454 |
| Spermaceti | 128.9 (average) | 435.2 |
| Beeswax | 94.5 (average) | 593.6 |

The numbers in the last column designated as "saturation equivalents" represent the number of grammes of the oil or fat in question that would be decomposed by one equivalent of potassium hydrate in grammes, and is obtained by dividing the percentages of potassium hydrate required into 5610, which is the molecular weight of KOH multiplied by 100. These saturation- or saponification-equivalents are quite characteristic for pure oils or fats, and allow of the recognition of adulteration in many cases.

The bromine and iodine absorption methods depend upon the percentage of bromine or iodine taken up by the oil under conditions intended to insure the formation of addition-compounds only. The fatty acids of the acetic or stearic series are saturated bodies, which do not form addition-compounds with bromine or iodine while the acids of the acrylic or oleic series combine with *two* atoms of a halogen, and, those of the propiolic or linoleic series, with *four* atoms of a halogen. The glycerides of the acids of these three series behave similarly to the free acids, so that the determination of the percentage of bromine or iodine assimilated gives a measure of the proportion of olein as against palmitin and stearin in a fat, and of the linolein of a drying oil as compared with the olein of a non-drying oil.

The bromine absorptions of various fixed oils have been determined by Mills and others (*Journ. Soc. Chem. Ind.*, ii. p. 435; iii. p. 366), the method of operating ultimately adopted being shortly as follows: About .1 gramme of the oil, previously deprived of all trace of moisture by heating or filtration through paper, is placed in a stoppered bottle of about one hundred cubic centimetres capacity, and dissolved in fifty cubic centimetres of carbon tetrachloride (carbon disulphide was first used), previously dried by calcium chloride. An approximately decinormal solution (eight grammes per litre) of bromine in dry carbon tetrachloride having an exactly known strength is

then added gradually to the solution of oil until there is, at the end of fifteen minutes, a permanent coloration. This is compared with a coloration similarly produced in a blank experiment, and thus a measure of the bromine-absorption is obtained. If great accuracy be desired, an excess of bromine may be used, aqueous solution of potassium iodide and starch added, and the solution titrated back with a standard solution of sodium thiosulphate.

A. H. Allen uses a modification of this process, which he terms the "moist bromine process," in which aqueous solutions are used.

The determination of the bromine value has been wholly superseded by Hübl's * method of ascertaining the iodine absorption value, which yields far more constant and reliable results. The bromine results, however, can be calculated if desired into iodine values by multiplication with $\frac{127}{80} =$ 1.5875. Hübl's procedure is as follows:

He employs an alcoholic solution of mixed iodine and mercuric chloride: twenty-five grammes of iodine are dissolved in one-half litre of alcohol, ninety-five per cent., free from fusel oil, and thirty grammes of mercuric chloride in another one-half litre of the same. The two solutions are then mixed after filtration, if necessary, and used after twelve hours' standing; it must also be standardized immediately before or after use. About .2 to .4 gramme of oils or .8 to 1 gramme of solid fats is weighed off and dissolved in ten cubic centimetres of chloroform; twenty cubic centimetres of iodine solution are added, and successive additions of five or ten cubic centimetres are made until, after two hours, the solution has a dark brown tint. It is best to leave it for from four to six hours protected from the light before the next step. From ten to fifteen cubic centimetres of a ten per cent. aqueous solution of potassium iodide are then added and one hundred and fifty cubic centimetres of water. The free iodine is then titrated with a solution of sodium thiosulphate containing twenty-four grammes per litre. The amount of iodine absorbed is calculated into units per cent. of the fat, and may conveniently be termed the iodine degree. This number appears to be tolerably constant for each oil, or class of oils, and is highest with the vegetable drying oils, as will be seen by this short list taken from Hübl's table: linseed oil, 158; hemp-seed oil, 143; cotton-seed oil, 106; olive oil, 82.8; lard, 59; palm oil, 51.5; tallow, 40; cocoa-nut oil, 8.9. The values thus obtained are quite constant, provided an excess of iodine of not less than thirty per cent. be employed and the operations be carried out under exactly the same conditions.

Hübl's method of iodine absorption has been found very useful in distinguishing the presence of cotton-seed oil in both lard and tallow. Thus, pure cotton-seed oil has an iodine absorption per cent. of 109.1, while pure tallow has only 40.8, and tallow with five per cent. of cotton-seed oil, 44; tallow with ten per cent. cotton-seed oil, 47.1; with fifteen per cent., 49.7; with twenty per cent., 52.9; with twenty-five per cent., 56.1; with thirty per cent., 59.2; and with forty per cent., 66 2.† In the analysis of lard, the case is somewhat complicated by the frequent admixture of beef stearine, as well as cotton-seed oil. Pure lard appears to have an iodine absorption per cent. of from fifty-seven to sixty-three, while beef stearine has only from twenty-three to twenty-eight per cent.‡

* Journ. Soc. Chem. Ind., iii. p. 641.
† R. Williams, Ibid., 1888, p. 187.
‡ J. Pattinson, Ibid., 1889, p. 31.

For qualitative detection only, cotton-seed oil can also be identified in lard by Becchi's test, with an alcoholic solution of silver nitrate, which gives a maroon color in the presence of the cotton-seed oil.

Bizio (*Atti del R. Instituto Veneto di Scienze*, iii. 6) states, however, that this coloration will be produced by any seed oil, olive oil among others.

The adulteration of the fatty oils very frequently calls for careful chemical investigation. The presence of soap, free fatty acids, etc., in them is of minor importance; the first, readily removable by washing with water after dissolving the oil-sample in carbon disulphide, and the second hardly to be called an adulteration, as free fat acids are normally present in many vegetable oils. The question as to whether they are present may be settled by Jacobsen's method of adding a little rosaniline to the oil. If free fatty acids are present, the oil turns red in color in consequence of the formation of rosaniline oleate. More important is the adulteration with resin and with hydrocarbon oils. In the absence of free fatty acids, resin may be isolated from fixed oils by agitating the sample with moderately-strong alcohol, separating the spirituous solution and evaporating it to dryness. The separation of the resin acids from free fatty acids is best effected by a method proposed by T. S. Gladding (*Amer. Chem. Journ.*, iii., No. 6), which is based upon the ready solubility of silver resinate in ether, and the almost complete insolubility of silver oleate, etc., in the same menstruum, even in the presence of a small quantity of alcohol. For details, the reader is referred to the original article. Hydrocarbon oils may generally be determined by saponifying the sample with alcoholic potash (five grammes oil, two grammes caustic potash, and twenty-five cubic centimetres ninety per cent. alcohol). The soap so obtained is mixed with clean sand, the alcohol evaporated over the water-bath at a temperature of not over 50° C., and the residue extracted with ether or petroleum spirit. From this solution, on evaporation of the solvent, will be gotten any hydrocarbons present.

An outline method of analyzing fatty oils containing foreign mixtures, due to Allen,* is given on the following page.

The analysis of soaps is a most important matter, as with the varying composition of soaps, shown on page 72, a control is absolutely necessary for those using or purchasing in quantity. One of the most satisfactory schemes for a complete soap analysis is that of A. R. Leeds, which is given on page 85. A similar one, agreeing with that of Leeds in general outlines, is given by Allen † in his excellent work on "Commercial Organic Analysis." In the water determination, great care must be taken to heat gradually at not too high a temperature at first (40° to 50° C.), and then slowly to increase to 100°, and continue until no further loss of weight is observed.

The separation of the mixed fatty acids is usually only effected in the mechanical way described in connection with stearic acid. (See p. 67.) An exact chemical separation of these higher fatty acids is hardly possible. The most satisfactory method known is that of Heintz (*Journ. für Prac. Chem.*, lxv. i.), based on the fractional precipitation of the alcoholic solution of the acids with magnesium acetate. This salt precipitates acids of the stearic series more easily than it does oleic acid and its homologues, and of the different homologues of the stearic series those of the highest molecular weights are thrown down first.

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* Allen, Commercial Organic Analysis, 2d ed., ii. p. 87.
† Ibid., p. 251.

## Outline Method of Analyzing Fatty Oils containing Foreign Admixtures.

**From 5 to 10 grammes weight of the sample (previously melted, if necessary) is passed through a dry filter, unless already perfectly clear.**

<table>
<tr>
<td rowspan="5">RESIDUE<br>may contain salt, curd, water, sand, and insoluble matters generally. It may be washed with ether, dried and weighed; then ignited and weighed again: the difference being the organic matter.</td>
<td colspan="5">THE CLEAR OIL is agitated in a stoppered separator with water* and ether, or recently-distilled carbon disulphide. The aqueous liquid is separated, and the oil solution again shaken with water if the previous treatment was found to remove anything.</td>
</tr>
<tr>
<td rowspan="4">AQUEOUS LIQUID<br>may contain soaps of the light metals. It is evaporated to dryness at 100° C., and the residue weighed and further analyzed if desired.</td>
<td colspan="4">OIL SOLUTION. Agitate with dilute sulphuric acid and separate.* Wash residual oil repeatedly by agitation with water till the aqueous liquid no longer reddens litmus.</td>
</tr>
<tr>
<td rowspan="3">ACID LIQUID<br>may contain sulphates of aluminum and heavy metals, previously existent as soaps.</td>
<td colspan="3">SOLUTION OF OIL in ether or carbon disulphide. Distil off the solvent and heat the residual oil with alcohol and a few drops of solution of phenol-phthalein. Then add standard soda cautiously, agitating the whole, between each addition, until a pink color is obtained, which remains after shaking. Note the volume of soda solution required, as the quantity used is a measure of the free fatty and resin acids, and will determine the necessity of looking further into their nature. Separate any undissolved oil, dilute the alcoholic liquid, evaporate off the alcohol at a gentle heat, and agitate with petroleum spirit; separate, evaporate off solvent, and add any separated oil to the main portion.</td>
</tr>
<tr>
<td rowspan="2">AQUEOUS LIQUID.<br>Add hydrochloric acid and agitate with ether or carbon disulphide. Evaporate the ethereal layer at 100°, and weigh residue representing mixed free fatty and resin acids of original sample, and, if soaps of aluminum or heavy metals were present, of the fatty acids resulting from their decomposition.</td>
<td colspan="2">OIL. Saponify with alcoholic potash. Boil off alcohol, dissolve soap in warm water, and agitate cooled solution with ether. Separate and agitate aqueous liquid a second and third time with ether.</td>
</tr>
<tr>
<td>AQUEOUS LIQUID<br>contains the glycerine and soap formed by the saponification of the neutral fixed oil of the sample. If the solution be treated with hydrochloric acid and agitated with ether, the weight of the fatty acids left on evaporating the ethereal layer, multiplied by 1.055, will give, approximately, the weight of the neutral fixed oil.</td>
<td>ETHEREAL LIQUID<br>distilled at 100°, and the last traces of the solvent removed by a current of air or other means, leaves the hydrocarbon oils in a state fit for identification and further examination.</td>
</tr>
</table>

* If an aliquot portion of the oil solution is not blackened by sulphide of ammonium, and leaves no ash on ignition, thus proving the absence of any metallic compounds, the treatments with water and sulphuric acid may be advantageously omitted.

## LEED'S SCHEME FOR SOAP ANALYSIS.

Weigh out 5 grammes. Dry at 100° C. Loss corresponds to *water*.

Treat with petroleum-ether.

- **EXTRACT** is *uncombined fat*. Dry at 110° and weigh.
- **RESIDUE** is soap and mineral constituents. Treat with alcohol.
  - **EXTRACT** is soap (fatty anhydride, resin, and combined alkali), glycerine, and free alkali. Add two or three drops of phenol-phthalein. If necessary, titrate with normal sulphuric acid.
    - Sulphuric acid used corresponds to *free alkali*. Calculate as NaOH.
    - Add a large excess of water and boil off the alcohol. Decompose with excess of normal $H_2SO_4$. Boil, filter, and wash.
      - **FILTRATE.**—*Combined soda* and *glycerine*. Titrate with normal soda solution.
        - Sulphuric acid used corresponds to *combined soda* in the soap. Calculate as $Na_2O$.
        - After titration evaporate to dryness on the water bath. Treat with absolute alcohol. Evaporate the alcoholic solution to dryness in a tared dish, and weigh as *glycerine*.
      - **RESIDUE.**—*Fatty acids* and *resin*. Dry at 110° and weigh. Dissolve an aliquot part in 20 c.c. strong alcohol, and using phenol-phthalein as an indicator, saponify with soda in slight excess. Boil, cool, and add ether to 100 c.c. Decompose with silver nitrate by adding in fine powder and shake well for ten minutes. Allow to settle.
        - Precipitate is stearate, palmitate, and oleate of silver.
        - **SOLUTION.**—Resinate of silver. Filter 50 c.c. from the total 100 c.c. Decompose with 20 c.c. of HCl (1 : 2). Allow the silver chloride to settle and evaporate an aliquot part of the ethereal solution in a tared dish. Dry at 110° and weigh. After applying correction for oleic acid, the weight corresponds to the *resin*. This weight subtracted from the combined weight of fatty acid and resin gives the *fatty acids*.
  - **RESIDUE.**—Sodium carbonate, chloride, sulphate and silicate, starch, and insoluble residue. Wash with 60 c.c. of water.
    - **FILTRATE.**—Sodium carbonate, chloride, sulphate, and silicate. Divide into 4 eq'l parts.
      - **Sodium Carbonate.**—Titrate with normal sulphuric acid, and calculate as $Na_2CO_3$.
      - **Sodium Chloride.**—Titrate with silver nitrate or weigh as silver chloride. Calculate as NaCl.
      - **Sodium Sulphate.**—Weigh as barium sulphate. Calculate as $Na_2SO_4$.
      - **Sodium Silicate.**—Decompose with HCl and determine the soda combined in silicate and the silica.
    - **RESIDUE.**—*Starch* and *insoluble residue*. Dry the filter and weigh. The weight is the starch and insoluble residue.
      - **STARCH.**—Convert the starch into glucose. Titrate with Fehling's solution. Subtract the weight of the *starch* so found, and the difference is the *insoluble mineral constituents*.

Commercial glycerine is seldom free from contamination, and a variety of impurities are liable to be present. The impurities of raw glycerine are much greater in number and amount than those present in the distilled product, and of the former, glycerine from soap lyes is much more impure than the product resulting from the autoclave process. Thus the mineral matter remaining as ash in the case of a distilled glycerine never amounts to more than .2 per cent., while in raw glycerine from soap lyes the ash usually ranges from seven to fourteen per cent., and in that from the autoclave process considerably less. The ash will contain common salt, and with it may be the chlorides and sulphates of lead, iron, zinc, magnesium, and calcium. In glycerine from soap lyes, sulphates particularly are present. They may be accompanied by thiosulphates, sulphites, and sulphides resulting from the sulphuric acid saponification of fats. Such glycerines are purified only with great difficulty.

Precipitation with basic acetate of lead often serves to distinguish between a distilled and an undistilled glycerine. This treatment removes rosin, while rosin oil and free fatty acids are removed by shaking up the sample with chloroform. The direct determination of the amount of true glycerine in commercial samples can be effected with moderate accuracy by the method of oxidation with potassium permanganate in alkaline solution, whereby the glycerine is oxidized to oxalic acid, which is then determined as calcium salt. For details, the reader is referred to Allen's "Commercial Organic Analysis," 3d ed., vol. ii., Part i., p. 314.

More accurate is said to be the "*acetin*" method of Benedikt & Cantor, which depends upon the quantitative formation of glyceryl triacetate when glycerine is heated with acetic anhydride. It is carried out as follows: 1 to 1.5 grammes of the crude glycerine is heated with seven or eight grammes acetic anhydride and about three grammes anhydrous sodium acetate for one to one and a half hours with inverted condenser; it is allowed to cool, fifty cubic centimetres of water are added, and the heating with inverted condenser continued until it begins to boil. When the oily deposit at the bottom of the flask is dissolved the liquid is filtered from impurities, allowed to cool, phenol-phthalein added, and dilute caustic soda (about twenty grammes per litre) run in until neutrality is obtained. Care must be taken not to exceed that point, or glyceryl triacetate is easily saponified. Twenty-five cubic centimetres of strong caustic soda (about ten per cent. strength) are now added from a pipette. The mixture is then heated for fifteen minutes and the excess of alkali titrated back with normal or half-normal hydrochloric acid. The strength of the alkali used is then determined by measuring twenty-five cubic centimetres with the same pipette and titrating it with the same acid. The difference in the two titrations gives the amount of alkali consumed in saponifying the glyceryl triacetate, and from this the glycerine can be calculated.

Various methods have been proposed for the analysis of nitro-glycerine, based upon its decomposition by different reagents. One of the simplest and most satisfactory is that proposed by Lunge, who uses for this purpose his nitrometer. (See p. 300.) An accurately-weighed quantity, varying from .12 to .35 gramme, according to the proportion of nitro-glycerine and the capacity of the apparatus, is introduced into the cup of a nitrometer filled with mercury. About two cubic centimetres of concentrated sulphuric acid is then added, and when the nitro-glycerine is dissolved the solution is allowed to enter the nitrometer through the tap. The cup is rinsed with

successive portions of two cubic centimetres and one cubic centimetre of strong sulphuric acid, which are allowed to enter as before, and the contents of the nitrometer are then thoroughly agitated in the usual way, and the volume of nitric oxide evolved read off after standing about fifteen minutes. The volume of gas in cubic centimetres at the standard pressure and temperature, multiplied by 3.37, gives the weight of nitro-glycerine in milligrammes. Hempel states that the total volume of five cubic centimetres of sulphuric acid must not be departed from; with less than that volume the reaction proceeds too slowly, and with more the results are too low.

In the analysis of dynamite, the nitro-glycerine may be conveniently determined by exhausting the dried sample with anhydrous ether, preferably in a Soxhlet tube (see p. 79), and weighing the insoluble residue. The nitro-glycerine is estimated from the loss, and, in the absence of other substances soluble in ether, such as camphor, resin, etc., this is the most satisfactory way. A complete scheme for the analysis of all nitro-glycerine preparations will be found in Allen, 3d ed., vol. ii., Part i., p. 339.

## V. Bibliography and Statistics.

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## STATISTICS.

1. Of Oils, Fats, and Waxes.—Of the production of the various vegetable and animal oils, fats, and waxes the figures are fragmentary. While they do not always give a proper view of these industries, they will suffice to indicate in a general way the degree of their development.

*Cocoa-nut Oil.*—The annual yield of nuts in Ceylon may be taken at 1,100,000,000. In 1898 the exports of cocoa-nut oil from this island amounted to 435,000 hundredweight, and in 1899 to 400,000 hundredweight, besides large quantities of "copra" (the dried pulp of the cocoa-nut) and cocoa-nuts. Large amounts are also exported from the Eastern Archipelago, from British India, and from the Pacific Islands. The nuts are also exported from the West Indies, from Central America, and from Brazil.

The English importations of cocoa-nut oil in recent years have been:

| Year | Quantity | | Value |
|---|---|---|---|
| 1895 | 285,016 cwt., | valued at | £321,550 |
| 1896 | 219,204 " | " " | 249,633 |
| 1897 | 242,731 " | " " | 265,068 |
| 1898 | 307,101 " | " " | 344,108 |
| 1899 | 458,297 " | " " | 545,642 |

*Palm Oil.*—The exportation of palm nuts from Southern Africa, accord- to Dr. von Scherzer, reaches 1,300,000 metric centners annually, of the greater part goes to France. The exportation of nuts from India, Siam, Cochin-China, China, South-Sea Islands, and Brazil r amounts to 600,000 metric centners.

e English importations of palm oil in recent years have been:

| Year | Quantity | | Value |
|---|---|---|---|
| 1895 | 1,262,933 cwt., | valued at | £1,320,690 |
| 1896 | 1,146,391 " | " " | 1,204,679 |
| 1897 | 973,108 " | " " | 1,001,368 |
| 1898 | 910,900 " | " " | 975,447 |
| 1899 | 945,472 " | " " | 1,037,265 |

*il* is produced chiefly in Mediterranean lands and in the East. der olive culture in Italy is now 2,258,000 acres. The oil 1885 was stated to be 3,338,825 hectolitres. The export of

olive oil from Italy ranges from 50,000,000 kilos. to 92,000,000 annually, according to the crop of olives (Simmonds's Tropical Agriculture, p. 394). Spain has some 2,500,000 acres devoted to olive culture, and the average annual production of oil for the last five years has been 2,976,384 metric centners. Of this the home consumption, for food, lighting, soap-making, etc., took 2,754,064 metric centners, leaving 222,320 metric centners for export. France had, a few years ago, 317,800 acres of olives under cultivation, producing 7,318,352 bushels of fruit and 392,618 hundredweight of oil. The total Greek export in 1875 was 12,244,615 okes (of 2.83 pounds). The Algerian production in 1877 was 55,239,000 kilos. of fruit, yielding 1,543,400 hectolitres (of twenty-two gallons) of oil. (Spon.) The exportation of Turkey and the Turkish provinces is estimated at 900,000 metric centners annually. (Heinzerling.)

The importations of olive oil into France is estimated at 20,000,000 kilos. annually, and the exportation at 5,000,000 kilos. (Schaedler.)

The English importations of olive oil for recent years have been as follows:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Olive oil in tuns (252 wine gals.) | 14,834 | 18,853 | 15,440 | 18,044 | 15,930 |
| Valued at . . . . . . . . | £522,811 | £612,876 | £515,531 | £608,122 | £553,286 |

The United States importations of olive salad oil have been as follows:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Gallons . . . . . | 775,046 | 942,598 | 928,567 | 736,877 | 930,042 |
| Valued at . . . | $952,405 | $1,107,049 | $1,134,077 | $923,804 | $1,090,250 |

*Corn Oil.*—Within the last few years corn oil has become an important article of export. The figures are as follows:

| | | |
|---|---|---|
| 1898 . . . . . . . . . . . . . . . . . | 2,646,500 gallons, valued at | $575,646 |
| 1899 . . . . . . . . . . . . . . . . . | 2,360,623 " " | 565,293 |

*Rape* or *colza oil* is cultivated in Germany, France, Austria, Hungary, Russia, Roumania, and India. The area in Germany planted with the different varieties of *brassica* amounted in 1882 to 445,000 acres, the crop of rape seed to 1,882,000 metric centners, valued at 50,500,000 marks. The importations of rape seed into Germany were in 1882, 681,000 metric centners, and in 1883, 1,154,290 metric centners. After deducting the seed for sowing, some 2,500,000 metric centners were available for oil production, and from this 900,000 to 1,000,000 metric centners of oil, valued at 48,000,000 to 56,000,000 marks, and 1,300,000 metric centners of oil-cake, valued at 17,000,000 marks, were obtained.

England imports some 800,000 metric centners of rape seed annually, and produces quite an amount. Austria presses for oil about 550,000 metric centners of rape seed annually, obtaining 200,000 to 225,000 metric centners of oil. The total consumption of rape and colza oil in Europe is estimated at 2,800,000 to 3,000,000 metric centners per annum, valued at 170,000,000 to 175,000,000 marks. (Heinzerling.)

The exportation of rape seed from Russia in 1879 amounted to 1,294,728 bushels, and from Roumanian ports, on the Danube, in 1878, to 938,376 bushels. The shipments from India in recent years have been as follows:

| 1885. | 1886. | 1887. |
|---|---|---|
| 4,521,933 cwt. | 3,721,840 cwt. | 2,664,693 cwt. |

*Sesamé Oil.*—The seeds come chiefly from the East Indies and the Levant, and the oil is pressed in Marseilles and Trieste. British India exported in 1885, 2,646,484 hundredweight; in 1886, 1,759,343 hundredweight; and in 1887, 2,121,119 hundredweight. France imports somewhat more than 1,000,000 metric centners; England, 250,000 metric centners; Italy, 150,000 metric centners; and Germany, 140,000 metric centners of sesamé seeds.

*Ground-nut Oil.*—The ground-nut (pea-nut), while indigenous to America, is now cultivated, for the oil it contains, in Africa, India, the West Indies, and Brazil. The American production, located chiefly in the States of North Carolina, Virginia, and Tennessee, amounts to an average of 3,500,000 bushels, or 77,000,000 pounds. The production of 1899 exceeded the average, amounting to 4,500,000 bushels. The average production of "Spanish pea-nuts" in the United States amounts to 16,500,000 pounds. About 400,000,000 pounds are annually exported from India and Africa, of which about half goes to Marseilles to be expressed for oil. The importations at Marseilles, where the oil is chiefly extracted, have been for the last few years:

| | Shelled. | Unshelled. | Total. |
|---|---|---|---|
| 1897 . . . . . . . . . . . . | 8,355 tons. | 31,888 tons. | 40,243 tons. |
| 1898 . . . . . . . . . . . . | 5,466 " | 63,286 ". | 68,752 " |
| 1899 . . . . . . . . . . . . | 9,579 " | 61,241 " | 70,820 " |

It is estimated that 3,250,000 bushels are annually eaten in the United States.

*Cotton-seed Oil.*—In the United States, it is reckoned that for each one pound of ginned cotton there are two pounds of seed. As the cotton crop of 1898 was 11,189,205 bales of 470 pounds, or 5,258,926,350 pounds, the production of seed must have been about 10,517,852,700 pounds, or some 4,695,470 tons. About one-third of this is required for sowing. The balance, 3,130,313 tons of crude seed, when hulled, would yield about 1,750,000 tons of hulled seeds. Each ton of hulled seeds yields 45 gallons of crude cotton-seed oil and 800 pounds of cotton-seed cake.

Of this annual production of crude cotton-seed oil, perhaps one-fourth goes into the production of "compound lard," and the rest is partly exported as cotton-seed oil, partly used in admixture with drying oils, and partly as soap-stock.

The exportations of cotton-seed oil from the United States for the last few years have been as follows:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| [Co]tton-seed oil in gallons . | 21,187,728 | 19,445,848 | 27,198,882 | 40,230,784 | 50,627,219 |
| Valued at . . . . . . | $6,813,313 | $5,476,510 | $6,897,361 | $10,137,619 | $12,077,519 |

In Europe, England is the chief country extracting the oil from the cotton seed, which comes chiefly from Egypt. The imports of seeds into England for 1886 were 255,701 tons; for 1887, 276,570 tons; for 1888, 255,500 tons.

*Hemp-seed oil* is produced chiefly in Russia. The exports of hemp seed from Riga in 1878 were 629,520 bushels, and in 1879, 725,809 poods (of thirty-six pounds) of seed and 573 poods of the oil. (Spon's "Encyclo-

*Linseed Oil.*—The supplies of linseed come from all countries, but most largely from Russia, the United States, and India. The world's crop of linseed in recent years has been as follows:

| | 1896. Bushels. | 1897. Bushels. | 1898. Bushels. |
|---|---|---|---|
| Russia | 39,625,000 | 27,296,500 | 28,537,500 |
| United States | 17,402,000 | 11,000,000 | 18,500,000 |
| British India | 14,795,000 | 8,839,000 | 17,839,000 |
| Argentina | 7,500,000 | 7,000,000 | 9,000,000 |
| Austria | 743,000 | 724,000 | 802,000 |
| Roumania | 674,000 | 676,000 | 461,000 |
| Belgium | 394,000 | 350,000 | 400,000 |
| France | 523,000 | 524,000 | 357,000 |
| Mexico | 108,000 | 222,500 | 311,000 |
| Netherlands | 312,000 | 275,000 | 308,000 |
| Manitoba | 267,500 | 255,500 | 305,500 |
| Hungary | 271,000 | 278,000 | 301,000 |
| Sweden | 70,000 | 73,500 | 75,000 |
| | 82,684,500 | 57,514,000 | 77,197,000 |

In 1895, 4,166,222 bushels of linseed, valued at $4,554,484, were imported into the United States. This dropped off to less than one-fifth the following year, and has since almost ceased. In 1897, 4,713,747 bushels, valued at $3,850,835, were exported, and again in 1899, 2,830,991 bushels, valued at $2,815,449.

*Oil-cake and Oil-cake Meal.*—The exportations of vegetable oil-cake from the United States have been during recent years as follows:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Cotton-seed cake (lbs.) | 489,716,053 | 404,937,291 | 623,386,638 | 919,727,701 | 1,079,993,479 |
| Valued at | $4,310,128 | $3,740,232 | $5,515,800 | $8,040,710 | $9,253,398 |
| Linseed cake (lbs.) | 243,936,442 | 393,429,432 | 433,106,448 | 436,206,321 | 487,177,390 |
| Valued at | $2,855,459 | $4,209,415 | $4,095,244 | $4,540,824 | $5,277,744 |

*Fish Oils.*—The amounts of sperm, whale, and fish oils of all kinds obtained annually, according to Mulhall,* are: sperm and whale oil, 1,485,000 hectolitres (32,670,000 gallons); fish oils of other kinds, 1,170,000 hectolitres (25,740,000 gallons), and oil from sea-birds, 58,500 hectolitres (1,287,000 gallons).

The English importations of train and other fish oils during the last few years were:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Amount in tuns | 24,597 | 21,961 | 18,129 | 20,673 | 20,358 |
| Valued at | £406,448 | £366,279 | £280,977 | £350,348 | £346,996 |

The exportations of whale and fish oils from the United States for the last five years have been:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Gallons | 769,179 | 844,125 | 853,340 | 669,227 | 1,026,125 |
| Valued at | $198,767 | $196,701 | $176,285 | $145,920 | $227,312 |

*Cod-liver Oil.*—The annual production of Newfoundland is said to amount to 1,250,000 gallons, valued at £200,000.

The Norwegian cod-liver oil production from the three districts of

* Mulhall, Production and Consumption, p. 142.

Lofoten, Romsdal, and Lodde is thus given on the authority of F. P. Möller (Cod-liver Oil and Chemistry, London, 1895):

| YEAR. | Number of fish. | Barrels of common liver oil. | Barrels of steam-prepared liver oil. |
|---|---|---|---|
| 1890 | 51,614,000 | 58,535 | 21,173 |
| 1891 | 40,880,000 | 33,815 | 22,331 |
| 1892 | 44,212,000 | 47,051 | 16,331 |
| 1893 | 47,738,000 | 41,851 | 18,757 |
| 1894 | 52,484,000 | 34,670 | 21,294 |

*Spermaceti and Sperm Oil.*—The production of spermaceti in the American whale-fisheries was 1,300,959 gallons in 1878, and 1,285,454 gallons in 1879. The exports of sperm oil from New York in 1878 were 912,603 gallons, and in 1879, 1,089,137 gallons. (Spon's "Encyclopedia.") The exportations of sperm oil have much diminished in more recent years. Thus, the exports for 1889 and 1890 were given as 98,823 gallons and 162,565 gallons respectively, valued at $69,628 and $124,601, and have since ceased almost entirely.

*Lard and Lard Oil.*—The production of lard in the United States during recent years is thus given by the *Cincinnati Price Current:*

| 1884-85. Pounds. | 1885-86. Pounds. | 1886-87. Pounds. | 1887-88. Pounds. | 1888-89. Pounds. | 1889-90. Pounds. |
|---|---|---|---|---|---|
| 480,405,000 | 514,230,000 | 527,032,000 | 487,179,000 | 483,902,000 | 624,227,000 |

Of this production from one-third to one-half is "compound lard," or lard admixed with cotton-seed oil and beef stearine.

The exports of lard from the United States during recent years have been as follows:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Pounds | 474,895,274 | 509,534,256 | 568,315,640 | 709,344,045 | 711,259,851 |
| Valued at | $36,821,508 | $33,589,851 | $29,126,485 | $39,710,672 | $42,208,465 |

Of this amount approximately one-third goes to Great Britain and Ireland and one-third to Germany.

The exports of lard oil during the same years were:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Gallons | 553,421 | 833,935 | 961,407 | 775,102 | 917,007 |
| Valued at | $304,093 | $426,401 | $419,803 | $305,825 | $412,447 |

*Tallow.*—The production of tallow for all European countries for the year 1882, according to Mulhall,* amounted to 355,700 tons, for the United States to 330,000 tons, and all other countries, 60,000 tons, making a total of 745,700 tons. The exportations of Russian tallow have greatly diminished in recent years; they were 40,300 tons in 1860, 21,100 tons in 1870, and 10,400 tons in 1880. The exportations from the United States, River Plate in South America, and Australia, on the other hand, have increased, especially the first and the last of these. In the year 1883 the exportations of tallow were as follows: From the United States, 45,000 tons; from Australia, 28,000 tons; from Argentine Republic, 10,500 tons, and from Uruguay, 12,000 tons. (Heinzerling.)

* Mulhall, Dictionary of Statistics, p. 434.

The exportations from the United States in recent years have been:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Pounds . . . | 25,864,300 | 52,759,212 | 75,108,834 | 81,744,809 | 107,361,009 |
| Valued at . | $1,293,059 | $2,323,764 | $2,782,595 | $3,141,653 | $4,367,356 |

The English importations of tallow and stearine during the same period have been:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Hundredweight . | 2,175,822 | 2,049,749 | 1,950,975 | 2,021,921 | 2,061,187 |
| Valued at. . . | £2,575,071 | £2,178,652 | £1,870,289 | £2,066,433 | £2,380,931 |

*Chinese or Insect Wax.*—The amount annually produced is valued by Professor Thistleton Dyer, of Kew Gardens, England, at £600,000.

*Carnauba Wax.*—The exportation of this wax from Brazil was estimated in 1876 at 871,400 kilos., valued at £162,500.

*Japan Wax.*—The exportations from Japan were in 1872, 1,230,588 kilos.; in 1873, 1,520,751 kilos., and in 1874, 1,302,465 kilos. The London importations in 1880 were 564,000 kilos., and in 1881, 666,660 kilos.

*Soaps.*—Sir Henry Roscoe stated, in 1881, in his inaugural address before the Society of Chemical Industry, that the annual production of soap in Great Britain and Ireland was about 250,000 tons. In a report on the exhibits at the Paris Exposition of 1878, it was stated that the French soap-trade had been for some time stationary at about 220,000 tons per annum, but was then declining.

The English export of soaps for the last five years has been:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Hundredweight . . | 728,398 | 719,651 | 738,564 | 805,665 | 930,827 |
| Valued at . . . | £756,704 | £744,848 | £762,248 | £831,207 | £942,269 |

The United States imports some soap (chiefly toilet and fancy grades) and exports a still larger amount (chiefly plainer grades). Thus, in recent years the values were:

| | 1897. | 1898. | 1899. |
|---|---|---|---|
| Imports . . . . . . . . . . | $766,376 | $498,512 | $576,197 |
| Exports . . . . . . . . . . | 1,136,880 | 1,390,603 | 1,457,610 |

*Glycerine.*—The total output of crude glycerine in the world is said to be 40,000 tons per annum, of which 14,000 tons are obtained in soap manufacture and 26,000 tons in stearine manufacture. The glycerine from these two sources is produced as follows:

| | From soap-making. | From stearic acid manufacture. |
|---|---|---|
| England . . . . . . . . . | 5500 tons. | 1200 tons. |
| France . . . . . . . . . | 3500 " | 6000 " |
| Germany . . . . . . . . | 2000 " | 3000 " |
| United States . . . . . . | 3000 " | 3000 " |
| Holland . . . . . . . . . | . . | 2000 " |
| Austria . . . . . . . . | . . . | 2000 " |
| Russia . . . . . . . . . | . . . | 2000 " |
| Belgium . . . . . . . . . | . . . | 1800 " |
| Italy . . . . . . . . . | . . . | 1800 " |
| Spain . . . . . . . . . | . . . | 1500 " |
| Other countries . . . . . . | . . . | 1700 " |

# CHAPTER III.

## INDUSTRY OF THE ESSENTIAL OILS AND RESINS.

### I. Raw Materials.

1. Essential Oils.—The essential or volatile oils, as they are termed, are found extensively distributed throughout the vegetable kingdom. They occur in almost all parts of the plants except the cotyledons of the seeds, in which, in general, the fixed or fatty oils are contained. The essential oils impart the peculiar and characteristic odors to the plants; they furnish us our perfumes, spices, and aromatics, and many of them possess valuable medicinal properties.

The essential or volatile vegetable oils are procured in several ways: (1) by distillation; (2) by absorption or "enfleurage"; (3) by means of solvents; (4) by expression; and (5) by maceration.

In the distillation method the plants are put into the still along with about an equal weight of water, either with or without previous soaking, and the distillation carried on rapidly. If necessary, the water that separates from the oil in the receiver is returned to the still and driven over a second or third time. The separation of the oil and water is effected in what is termed a "Florentine receiver," from the bottom of which the water can be siphoned off without disturbing the oily layer. The odors of some flowers, such as jessamine and mignonette, are too delicate to bear heat, and for these the process of absorption, or "enfleurage," as it is called in the south of France, is employed. Sheets of glass in wooden frames, called *chassis*, are coated on their upper and lower surfaces with grease about a tenth of an inch in thickness. The flowers are spread upon this grease, and a number of frames are superimposed on each other. After a day or two the flowers are carefully removed and replaced by fresh ones, and this is continued for two or three months, till the fat is impregnated with the odors. It is then removed and extracted with alcohol. Recently the grease has been replaced in some cases by soft paraffine, glycerine, or vaseline.

For the extraction by solvents, alcohol, ether, petroleum-naphtha, and notably carbon disulphide are employed, and the solvent recovered by distillation. The essential oils of lemons and oranges of commerce, and of some other fruits, are chiefly obtained by submitting the rind to powerful pressure. The oils are more fragrant but not so white as when distilled, and the process is only adapted for substances which are very rich in essential oils. Flowers with very delicate perfume, such as those of the bitter orange, violets, etc., which would be spoiled by distillation, are treated by this method. The medium used for infusion is clarified beef or mutton suet or lard. The fat is melted, the flowers immersed, and the mixture stirred occasionally for a day or so. The exhausted flowers are removed and fresh ones introduced, and such renewals are continued till it is judged that the fat is sufficiently charged with the oil.

The essential oils are usually more limpid and less unctuous than the fixed oils, but some of them, when in the crude state, may be quite thick or even semi-solid from admixtures of solid and crystalline ingredients with the more liquid portion. Their odor is that of the plants which yield them, and is usually powerful; their taste is pungent and burning. They mix in all proportions with the fixed oils, dissolve in both alcohol and ether, and are sparingly soluble in water, forming "perfumed" or "medicated water." They are not saponifiable. Their boiling-points usually range from 310° to 325° F. (154.5° to 162.7° C.), although in some oils the hydrocarbons boil at 356° F. (180° C.) or even higher. They are, however, capable in most cases of being distilled in a current of steam. In specific gravity they vary from oil of citron .850 to oil of winter-green 1.185 at 15° C.

Chemically, essential oils may be divided into the three great classes,—oils composed of hydrocarbons only; oils containing oxygenated compounds, and oils containing sulphur compounds. We will note briefly the more important illustrations of each of these three classes.

I. The oils which do not contain oxygen are composed of hydrocarbons of what is called the *terpene* series. These seem to be of a common formula, which is $C_{10}H_{16}$ or a multiple of this. We may distinguish several groups.

1. *Hemiterpenes*, $C_5H_8$.—A hydrocarbon of this formula is yielded when caoutchouc is destructively distilled.

2. *Terpenes*, $C_{10}H_{16}$.—The true terpenes. Of these some six or eight distinct compounds have been obtained, but they may exist in different physical modifications according as they are right or left rotatory or inactive to polarized light.

3. *Sesquiterpenes*, $C_{15}H_{24}$.—This group includes the hydrocarbons of oils of cedar, cubebs, and cloves.

4. *Diterpenes*, $C_{20}H_{32}$, includes colophene, obtained in the treatment of oil of turpentine, and possibly others.

5. *Polyterpenes*, $(C_{10}H_{16})_n$, includes the polymerized hydrocarbons of caoutchouc and gutta-percha.

II. The oils which contain oxygen may owe this to one of several classes of oxygen compounds.

1. *Camphors*.—This group includes common or Japan camphor, borneol, cineol, or eucalyptol, menthol. These bodies are either alcohols or ketones in chemical character.

2. *Unsaturated Alcohols and Aldehydes*.—A number of compounds of this class have recently been identified as constituting important odoriferous principles in oils. Thus, geraniol, or rhodinol and linalool (coriandrol) are unsaturated alcohols, while citral and citronellal are unsaturated aldehydes.

3. *Esters or Compound Ethers of Alcohols*.—The formic, acetic, and valeric ethers of borneol and the formic and acetic ethers of linalool and geraniol are all found natural in essential oils. Methyl salicylate is another compound ether, constituting the main constituent of oil of wintergreen.

4. *Phenols*.—Thymol, of oil of thyme, and carvacrol, of origanum oil, belong to this class.

5. *Ethers of the Phenols*.—Anethol, of anise oil, eugenol, of oil of cloves, and safrol, of oil of sassafras, belong here.

6. *Aromatic Aldehydes*.—Benzaldehyde, salicyl aldehyde, anisic aldehyde, vanillin, cumin aldehyde, and cinnamic aldehyde belong to this class.

III. The oils which contain sulphur seem to belong to two classes.

1. *Sulphides of Organic Radicals.*—Garlic oil, onion oil, leek oil, and similar oils contain allyl and vinyl sulphides.

2. *Sulphocyanates of Organic Radicals.*—Mustard oil and some others contain allyl sulphocyanate.

*Oil of Turpentine.*—This oil is produced by all the *Coniferæ* in greater or less amount. It flows from cuts in the tree as a balsam (see p. 97), known as turpentine. This, on distillation with steam, yields the volatile oil of turpentine, and there remains behind the resin (colophony resin) commonly known as "rosin." While a number of minor varieties of turpentine are known, such as Venetian, Hungarian, Strasburg, Chios turpentines, and Canada balsam, which are of pharmaceutical value, but three commercially important varieties of oil of turpentine need be noted. They are English or American oil of turpentine, from *Pinus australis* and *Pinus tæda*, collected in North and South Carolina and Georgia; the French oil of turpentine from *Pinus maritima*, collected in the neighborhood of Bordeaux; and the Russian or German oil of turpentine, from *Pinus sylvestris*. Of the American oil, only seventeen per cent. is obtained on distillation of the crude turpentine balsam; of the French, as much as twenty-five per cent. of oil may be obtained; and of the Russian, thirty-two per cent. The essential composition of all three of these oils, when rectified, is $C_{10}H_{16}$, but distinct hydrocarbons, differing in physical if not in chemical characters, are considered to be present in each of the three oils. Thus the terpene, $C_{10}H_{16}$, of French oil of turpentine is lævo-rotatory, and is known as *lævo-pinene*, while that of the American oil is dextro-rotatory, and is known as *dextro-pinene*. Otherwise they are practically identical in properties. Russian oil of turpentine consists mainly of a hydrocarbon, *sylvestrene*, which boils some sixteen to twenty degrees Centigrade higher than the others, and shows some other minor differences. The commercial oil of turpentine is a colorless, very mobile, highly refracting liquid, of pleasant odor when freshly rectified, but becoming disagreeable by exposure to the air, as it absorbs oxygen and becomes resinous. It is almost wholly insoluble in water, glycerine, and dilute alkaline and acid solutions. It is soluble in absolute alcohol, ether, carbon disulphide, benzene, petroleum spirit, fixed and essential oils. It is itself a solvent for sulphur, phosphorus, resins, fats, waxes, caoutchouc, etc.

Turpentine yields a number of interesting and medicinally important derivatives under the influence of different reagents. Thus, by the action of hydrochloric acid gas is formed *pinene hydrochloride*, $C_{10}H_{17}Cl$, known as "artificial camphor," because of its appearance and odor. When heated with soaps or weak alkali, it splits off hydrochloric acid again and leaves *camphene*, $C_{10}H_{16}$. When turpentine oil stands in contact with water, especially in the presence of nitric acid and alcohol, it unites with three molecules of water to form a hydrate, $C_{10}H_{18}(OH)_2 + H_2O$, known as *terpin hydrate*. This is in colorless rhombic prisms of slightly aromatic and somewhat bitter taste, melting at 116°–117°. When the anhydrous *terpin*, $C_{10}H_{18}(OH)_2$, obtained in this fusion is distilled with dilute sulphuric acid it loses a molecule of water and yields *terpineol*, $C_{10}H_{17}(OH)$, an oil of hyacinthine odor which is used in medicine. When sulphuric acid is allowed to stand in contact with oil of turpentine and the mixture after a day's standing is heated to boiling, the oil is changed into an optically inactive mixture of terpenes, known as *terebene*, which boils, according to the United States Pharmacopœia, at 156°–160°.

*Camphor.*—This is one of the most important of the oxidized principles which were referred to as accompanying the hydrocarbons in the crude essential oils. While the name is frequently used to designate a class of compounds, it is commercially restricted to the laurel camphor, $C_{10}H_{16}O$, which is obtained from the wood of the Japan camphor-tree (*Camphora officinarum*) by distillation with water and after purification with sublimation. It forms a colorless, translucent, tough, fibrous mass, but may be obtained crystallized in prisms. It has a peculiar, fragrant odor and burning taste. It melts at 347° F. (175° C.), and boils at 399.2° F. (204° C.). It is nearly insoluble in water, but readily soluble in alcohol, ether, acetone, carbon disulphide, chloroform, and oils.

*Borneol* (or Borneo camphor), *cineol* (or eucalyptol), *linalool*, and *geraniol* are camphors with the formula $C_{10}H_{18}O$. They occur either free or in the form of esters in many of the essential oils.

*Menthol*, $C_{10}H_{20}O$, is a white, camphor-like body found in peppermint oil, from which it may be chilled out. It is largely used in medicine and pharmacy.

*Thymol*, $C_{10}H_{14}O$, found in a number of essential oils, is a solid phenol.

2. RESINS.—The resins are products of the oxidation of the terpenes, and either accompany them in the crude essential oils or occur as exudations from trees hardening on exposure to the air. The classification of resins usually adopted at present is into (1) true resins, (2) gum resins, and (3) oleo-resins or balsams. The true resins are hard, compact products of oxidation, made up chiefly of what are termed "resin acids," which, admixed with fatty acids, are capable of saponifying with alkalies and yield "rosin soaps" (see p. 64); the gum resins differ from the true resins only in containing some gum capable of softening in water; and the oleo-resins include the mixtures of essential oil and resin of whatever consistency and the mixtures of benzoic and cinnamic acid and salts of these acids. This last class is obviously much the largest of the three. To the first class belong the hard resins, which serve for the manufacture of varnishes, such as copal, dammar, mastic, sandarach, dragon's blood, gum lac, and amber; to the second class, olibanum or frankincense, myrrh, ammoniacum, asafœtida, galbanum, and tragacanth; and to the third class, crude turpentine, benzoin, storax, copaiba, Peru and Tolu balsams. Brief mention will be made of a few of the commercially more important.

*Amber* is a fossil resin found in detached pieces on the sea-coast, and particularly in the blue earth along the Baltic coast of Prussia, between Königsberg and Memel. Its applications are chiefly as an article for the manufacture of mouth-pieces of pipes and cigar-holders and for beads, for the preparation of a superior varnish, and for the production of amber oil and succinic acid.

*Gum Arabic.*—This is included among gum resins because an exudation analogous to other resins, but is almost wholly a gum, soluble in water, and closely related chemically to the starch group. (See p. 168.) It is yielded by the different species of *Acacia*, and, at present, comes chiefly from Central and North Africa, by way of Egypt, Senegal, and the Red Sea. It varies greatly in purity and color, and is used, because of its mucilaginous character, for a multitude of applications, as in medicine, confectionery, preparation of textile fabrics, manufacture of inks, etc.

*Copal and Animé.*—These terms include a number of related resins, which are of both fossil and recent origin. The Zanzibar copal or animé is chiefly

fossil, and is dug out of the soil by the natives for some distance along the southeastern coast of Africa. Some freshly-exuded copal resin is also gathered here. On the west coast of Africa, for a distance of seven hundred miles, copal resin is also dug as a fossil. When of good quality it is too hard to be scratched by the nail, has a conchoidal fracture, and a specific gravity ranging from 1.059 to 1.080. Unlike others, the copal resins are soluble with difficulty in alcohol and essential oils, and this property, combined with their extreme hardness, renders them very valuable for making varnishes.

*Dammar* is obtained from the *Dammara orientalis*, a coniferous tree, indigenous in the East Indies and Moluccas, and also from *Dammara australis*, in New Zealand. The two varieties are known as East Indian and Australian dammar, the latter being also known as *Kauri* resin. The former is that commonly met with in commerce under the simple name of dammar. The resin occurs in masses, coated on the exterior with white powder from mutual attrition, while the interior is pale amber-colored and transparent. It is scratched by copal, but is harder than rosin. The resin splits and cracks at the temperature of the hand. The Kauri variety is chiefly fossil in its origin. The dammar is extensively used in the manufacture of varnishes.

*Lac* is a resinous incrustation produced on the bark of the twigs and branches of various tropical trees, by the puncture of the female "lac insect" (*Coccus lacca*). This crude exudation constitutes the *stick-lac* of commerce. *Shell-lac* or *shellac* is prepared by spreading the resin into thin plates after being melted and strained. In the preparation of the shellac, the resin is freed from the coloring matter, which is formed into cakes, and is known as "lac-dye." "Button-lac" differs from shellac only in form. Instead of being drawn over a cylinder, the melted lac is allowed to fall upon a flat surface, and assumes the shape of large cakes about three inches in diameter and one-sixth inch thick. *Bleached lac* is prepared by dissolving lac in a boiling lye of pearl-ash or caustic potash, filtering and passing chlorine through the solution until all the lac is precipitated. This is then collected, well washed, and pulled in hot water, and finally twisted into sticks and thrown into cold water to harden.

*Seed-lac* is the residue obtained after dissolving out most of the coloring matter contained in the resin. The common shellac is used in varnishes, lacquers, and sealing-wax; the bleached lac in pale varnishes and light-colored sealing-wax.

*Mastic* is the resin flowing from the incised bark of the *Pistacia lentiscus*, and comes exclusively from the Island of Chios, in the Mediterranean. It comes into commerce in pale, yellowish, transparent tears, which are brittle, with conchoidal fracture, balsamic odor, and softens between the teeth. It is soluble in alcohol, oil of turpentine, and acetone. It is used in varnish-making.

*Colophony Resin* (rosin) is the solid residue left on distilling off the volatile oil from the crude turpentine. The resins from the Bordeaux turpentine and that from the American turpentine are substantially identical. Rosin is a brittle, tasteless, very friable solid, of smooth, shining fracture, specific gravity about 1.08. It softens at 80° C. (176° F.), and fuses completely to a limpid yellow liquid at 135° C. (275° F.).

It is insoluble in water, difficultly soluble in alcohol, but freely soluble in ether, acetone, benzene, and fatty oils. With boiling alkalies it takes up

water to form abietic acid, and then unites with the alkali to form a rosin soap. (See p. 63.)

3. CAOUTCHOUC (India-rubber).—This is the chief substance contained in the milky juice which exudes when a number of tropical trees belonging to the natural orders *Euphorbiaceæ*, *Artocarpaceæ*, and *Apocynaceæ* are cut. This juice is a vegetable emulsion, the caoutchouc being suspended in it in the form of minute transparent globules. The emulsion is easily coagulated, and the caoutchouc caused to separate by the addition of alum, salt solutions, and other means

Caoutchouc belongs in the same general category as the essential oils, as it possesses the general formula $(C_{10}H_{16})_n$, and is, hence, a polymer of the terpene formula $C_{10}H_{16}$. On submitting it to destructive distillation it yields *caoutchin*, $C_{10}H_{16}$, boiling at 171° C., and *isoprene*, $C_5H_8$, boiling at 38° C.

The different species of rubber-trees are cultivated in Mexico, South America, and the West Indies, in the East Indies, Borneo, Sumatra, and the African coast.

The commercial varieties of caoutchouc may be grouped under four heads, the relative value of which accords with the order in which they are placed: *South American:* Para, Ceará, Carthagena, Guayaquil; *Central American:* West Indian, Guatemala; *African:* Madagascar, Mozambique, West African; *Asiatic:* Assam, Borneo, Rangoon, Singapore, Penang, and Java. The Para rubber (from the *Hevea Brasiliensis* or *Siphonia elastica*) is the best of the many varieties, and commands the highest price.

Caoutchouc, when pure, is nearly white, but the commercial varieties are discolored by smoke in the drying of the freshly-exuded juice in the methods usually followed. At ordinary temperatures caoutchouc is soft, elastic, and so glutinous that two freshly-cut surfaces pressed strongly together will permanently adhere. At low temperatures it is harder, is less elastic and adhesive, while, on heating it, the elastic property disappears also, and it becomes perfectly soft and can be kneaded. In water caoutchouc swells up without dissolving; in ether, petroleum-naphtha, benzene, carbon disulphide, oil of turpentine, rosin oil, and oils gotten by the dry distillation of the rubber itself, the caoutchouc swells up rapidly, and after a time dissolves to a greater or less degree. The best solvents are carbon disulphide and chloroform, and Payen recommends carbon disulphide, to which five per cent. of absolute alcohol has been added, as excellent. Caoutchouc is quite indifferent to most chemical reagents, but is attacked by strong nitric and sulphuric acids. Fatty matters present in the solvents used seem to have a deleterious action upon the caoutchouc, causing it to become first soft and afterwards hard and brittle. Caoutchouc softens at 120° C., melts at about 150° C., and decomposes at 200° C.

4. GUTTA-PERCHA AND SIMILAR PRODUCTS.—Gutta-percha is obtained from the milky juice of different trees of the genus *Isonandra*, belonging to the natural order *Sapotaceæ*. By the coagulation of the collected juice the gutta-percha globules mass together and can be kneaded into lumps. The localities in which the gutta-percha is cultivated are Borneo, Sumatra, and the Malayan Archipelago. It comes into commerce in irregularly- and fancifully-formed blocks. It forms a fibrous mass, varying in color from nearly white to reddish or brownish, looking something like leather clippings cemented together, and has a specific gravity of .979. At ordinary temperatures it is hard and somewhat elastic, at 25° C. (77° F.)

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it becomes soft, and at 50° C. (122° F.) it can be kneaded or rolled out into plates. Between 55° C. and 60° C. it is so thoroughly plastic as to be drawn into tubes, thread, plates, and at 120° C. (248° F.) it melts. Its elasticity seems distinctly greater in the direction of its fibre than in an opposite one, while caoutchouc is equally elastic in all directions. Gutta-percha is a poorer conductor of electricity than caoutchouc, and hence its extensive use in insulating wires and cables. Its power of softening at 45° C. is partly overcome by the process of vulcanization or union with sulphur. Chemically, gutta-percha seems to be composed, like caoutchouc, of a hydrocarbon $(C_{10}H_{16})_n$, but is always accompanied by a certain amount of oxidation products. Payen found that the crude gutta-percha, after thorough exhaustion with alcohol, left seventy-eight to eighty-two per cent. of a pure hydrocarbon, that he termed gutta, which, at from 15° C. to 30° C. (59° to 86° F.), was tenacious and ductile, but not very plastic.

*Balata* is the dried, milky juice of the bully-tree (*Sapota Milleri*), which flourishes in Guiana. The balata is obtained from the juice in a manner similar to gutta-percha. In its properties it is intermediate to caoutchouc and gutta-percha; it is more plastic and readily kneaded than the former and more elastic than the latter. At ordinary temperatures it is compact and horny, but at 49° C. already it becomes soft, and can be shaped. Towards solvents it behaves like gutta-percha.

It is used chiefly in England as a substitute for gutta-percha and caoutchouc, and is also used as an addition to these. Towards chloride of sulphur and metallic sulphides it acts like caoutchouc and gutta-percha.

5. Natural Varnishes.—This term is applied to a class of natural products which are resinous exudations, capable of direct use as varnishes or lacquers. The most important are:

(1) *Burmese lacquer*, a thick, grayish terebinthinous liquid, collected from the *Melanorrhœa usitatissima* of Burmah. It dissolves in alcohol, turpentine oil, and benzene, assuming greater fluidity. Locally, it is used in enormous quantities in lacquering furniture, temples, idols, and varnishing vessels for holding liquids.

(2) *Cingalese and Indian lacquer*, a black varnish obtained in Ceylon and India from *Semicarpus anarcardium*, and in Madras, Bombay, and Bengal, from *Holigarua longifolia*. It forms an excellent varnish, adhering strongly to wood and metal.

(3) *Japanese and Chinese lacquer* is derived from several species of *Rhus*, whose fruits form the Japan wax of commerce. (See p. 51.) It is purified by defecation and straining, and mixed with coloring matter, if needed. It is most extensively used in Japanese and Chinese lacquer-work.

## II. Processes of Treatment.

1. Manufacture of Perfumes and Similar Products.—In the use of essential oils or mixtures of them, as the basis of agreeable smelling preparations or perfumes, several classes of preparations may be distinguished: (1) Perfumed waters or alcoholic solutions of mixed essential oils; (2) odoriferous extracts or alcoholic extracts from fatty oils charged with odors by "enfleurage" or maceration; and (3) pomades and perfumed soaps. In the manufacture of the first class of preparations, the alcohol to be used must be free from fusel-oil and thoroughly deodorized. The essential oils may be in part dissolved separately in the alcohol or

added together to the proper quantity of the solvent according to the nature of the materials. Long-continued standing of the alcoholic solutions is now considered sufficient to effect a thorough amalgamation and development of the desired perfume, and distillation is dispensed with. As examples of such perfumes we have the well-known cologne waters and *eau de mille fleurs*.

The odoriferous extracts are gotten by treating with alcohol the fatty oils and fats which have been charged with the perfumes of flowers by the "enfleurage" process. Glycerine, soft paraffine, and vaseline have latterly been used too in the extraction of the odors. On chilling the alcohol by freezing mixtures or other means to 18° C., the fat is separated out and gotten rid of.

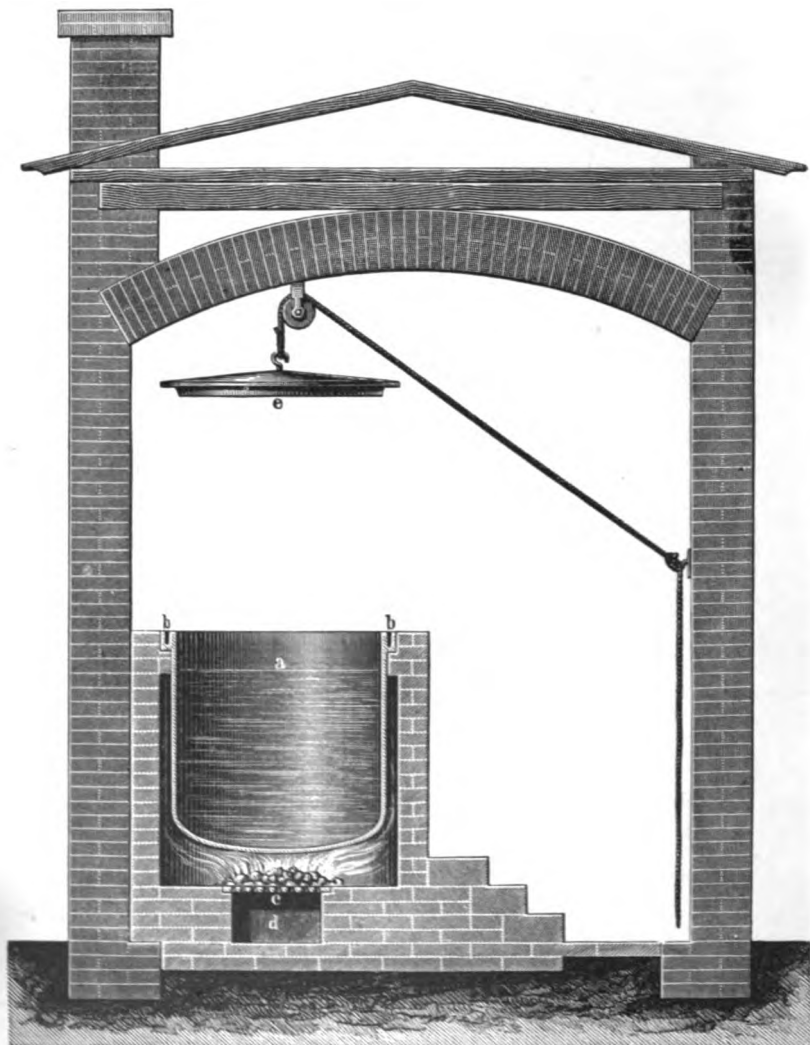
Pomades are made from fatty oils, the basis usually being oil of almonds, oil of ben, or olive oil. The processes for preparing these scented fats are those of infusion with warm fatty oils or melted fats at a temperature of about 65° C., and of "enfleurage," or cold perfuming, as already described. The analogous class of compounds, perfumed soaps, have been spoken of under another heading. (See p. 76.)

2. MANUFACTURE OF VARNISHES.—Very much more important, in an industrial sense, is this application of essential oils and resins. Under the name varnish is generally understood either a solution of a resin or a rapidly resinifying oil, which, when applied to solid bodies, becomes dry and hard, either by evaporation of the solvent or a drying and oxidation of the same, while the film of resin left behind makes a hard, glossy coating, impervious to air and moisture. Varnishes may be of three classes, according to the character of the solvent used for the resin: (1) Linseed-oil varnishes, in which boiled linseed oil is used; (2) spirit varnishes, in which alcohol or petroleum spirit is used; (3) turpentine-oil varnishes.

*Linseed-oil Varnishes.*—Linseed oil itself, as a drying oil (see p. 49), is capable of forming a varnish without the addition of a resin. For the preparation of varnish, the oil must first be boiled. When heated to 130° C. it begins to boil, but the heat is continued until it shows about 260° C. (500° F.), which temperature should not be much exceeded. It absorbs oxygen in this process and becomes thick and glutinous. The absorption of oxygen and the thickening of the oil are much accelerated by the use of driers like litharge, manganese dioxide, lead acetate, manganese borate, etc. (See p. 74.) Boiling linseed oil over free fire, as it is generally carried on, is illustrated in Fig. 34. Care should be taken that the kettle is not filled so full as to allow it to boil over when strongly heated. The lid *e*, ordinarily raised, can be lowered upon it if the escaping decomposition products catch fire.

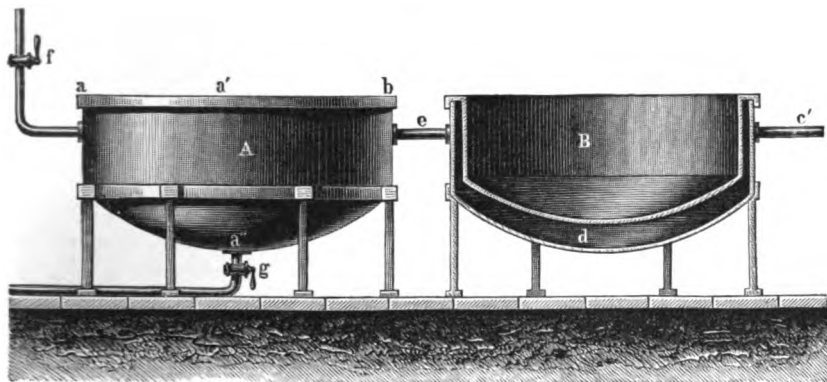
In Fig. 35 is shown a pair of kettles arranged for boiling the linseed oil by steam. Pressures of four and a half to five atmospheres are used for the steam in this case, and a temperature of 132° C. (269.6° F.) yielding a perfectly clear, light-colored varnish. When boiled so as to have lost one-twelfth of its weight it yields the ordinary boiled oil varnish; if heated until it loses one-sixth of its weight it becomes thicker and yields a stiff varnish, which is used as the basis of printer's ink. (See p. 104.) The specific gravity of boiled linseed oil of good quality varies from .940 to .950, and on ignition it leaves a mineral residue of from .2 to .4 per cent. Experiment has taught that oxidation proceeds the more rapidly when it is pushed rapidly; or, in other words, in order to change linseed oil into varnish by atmospheric exposure, it must be brought to boiling as rapidly as

possible. What takes place in this case is not an evaporation simply, but a decomposition of the linolein (glyceride of linoleic acid) takes place, whereby glycerine separates, and a portion of the linoleic acid changes into linoleic anhydride, $C_{32}H_{54}O_{31}$, an elastic and caoutchouc-like mass (see p. 111), which then dissolves in the undecomposed linseed oil and gives the oil its valuable varnish-forming and drying character. Another part of the

FIG. 34.

linoleic acid, liberated by the boiling, absorbs oxygen and changes into oxylinoleic acid, $C_{16}H_{26}O_5$, which at first is of turpentine-like character, while all undecomposed glyceride of linoleic acid dries up to elastic linoxyn, $C_{32}H_{54}O_{11}$. A good varnish, therefore, is made up of three factors: (1) Linoleic anhydride, (2) oxylinoleic acid, and (3) linoxyn.

These views of Mulder as to the changes which occur in the boiling of

linseed oil are controverted by Bauer and Hazura,* who consider that the liquid fatty acids of linseed oil consist of eighty per cent. of linolenic and isolinolenic acids ($C_{18}H_{30}O_2$), together with nearly twenty per cent. of linoleic acid ($C_{18}H_{32}O_2$), and small quantities of oleic acid ($C_{18}H_{34}O_2$). They con-

FIG. 35.

sider Mulder's oxylinoleic acid to have been a mixture, and state that the more linolenic acid an oil contains, the more quickly it dries.

The pure linseed-oil varnish so prepared may then serve for the preparation of what are termed lacquers or solutions of resins in linseed-oil varnish, thinned out ordinarily with turpentine oil or benzine. Of the resins, amber, copal, animé, dammar, and asphalt are used for these lacquers. In order to prepare these varnishes, the resins, amber, copal, etc., are fused in a kettle placed over a coal-fire in such a way that it sinks into the fire-chamber but a slight distance, and the flame can touch the bottom of the kettle only. After the resin has fused, the proper amount of boiling linseed-oil varnish is added, care being taken that the mixture does not fill the kettle to more than two-thirds at the most, and the contents then boiled for ten minutes. When the kettle has cooled down to about 140° C., the necessary amount of turpentine oil is added.

FIG. 36.

In the case of the two resins, amber and copal, something more than a fusion is essential. They are submitted to a dry distillation, and only after they have given off from ten to twenty per cent. of their weight in oily distillation products does the residue become perfectly soluble. A form of still in which this distillation of resins is carried out is shown in Fig. 36. The copper still *B*, which is heated in this case over the direct fire, is provided with

* Zeit. für Angew. Chem., 1888, pp. 455–458.

mechanical agitation, *R*, and a tube, *A*, for drawing off the melted residue. This tube is covered where it projects through the fire by fire-brick to protect it from the flame. The distillation products escape through *D* and are condensed by the worm *K*. The dry distillation of copal proceeds best at a temperature of 340° to 360° C., while that of amber requires 380° to 400° C. If heated higher than these temperatures the resins become dark. As the melting-point of lead is 334° C., a lead bath is recommended for the copal distillation.

These lacquers are the hardest and most durable of varnishes, but they dry more slowly than simple linseed-oil varnish.

*Spirit varnishes* are solutions of resins, such as sandarach, mastic, dammar, gum-lac, and shellac, in alcohol, although this is sometimes replaced by other solvents, such as methyl alcohol, acetone, and petroleum spirit. The spirit varnishes dry rapidly, leaving a brilliant surface, but are more apt to crack and peel off than turpentine varnishes. Turpentine is often added to these varnishes to diminish this brittleness. Among the most important varnishes of this class are shellac varnish, of which the finest grade is prepared from bleached shellac dissolved in alcohol, and copal varnish. In the preparation of this latter, the copal must be first fused, or rather submitted to dry distillation in the manner already described. (See p. 103.) The fused copal residue is afterwards powdered, mixed with sand and covered with strong alcohol, heated to boiling for some time and then filtered. The addition of elemi resin imparts a toughness to the copal varnish.

Colored spirit varnishes are made by the addition of alcoholic extracts of annatto, dragon's blood, gamboge, turmeric, cochineal, or even solutions of the different coal-tar colors.

*Turpentine-oil Varnishes.*—These are prepared in the same way as the spirit varnishes. They dry more slowly, but are more flexible and durable. The most important are copal varnish and dammar varnish. Turpentine and linseed oil are frequently used jointly in the preparation of varnishes, so as to obtain the best results. Thus, in the manufacture of copal and amber varnishes, described before (see p. 103), the relative amounts of materials are: Ten parts of copal or amber (or the residue from the distillation of amber oil), twenty to thirty parts of linseed-oil varnish, and twenty-five to thirty parts of oil of turpentine.

3. MANUFACTURE OF PRINTER'S INK.—Printer's ink, of whatever grade, whether for newspaper print, for book, lithographic, or copperplate printing, is a very stiff, rapidly-drying linseed-oil varnish, to which has been added lamp-black or charcoal in the finest state of division. For its preparation, linseed, poppy, or nut oil is heated in copper vessels, over a free fire to a temperature beyond the boiling-point, so that inflammable vapors are given off. These are frequently ignited, or, as is now preferred, they may be allowed to escape into a draught chimney. The heating is continued until the oil becomes quite thick and a film forms on the surface, which causes it swell up with escaping bubbles of vapor. A sample taken out and tested tween the fingers should draw out in long filaments. In this condition, th the addition of about sixteen per cent. of lamp-black, the varnish will y very easily and rapidly. If the varnish has not been boiled long enough, the printed characters will run together and oil will be absorbed in the paper fibre, so that the printed letters will show a yellowish border.

For the ink to be used in book-printing, an addition of soap is absolutely

necessary; it allows the inked type to be withdrawn from the moist paper clear and sharp without any adhering or smearing. The finer the printed work required the stiffer and more thoroughly boiled the varnish must be, so that for copperplate and lithographic inks a much stiffer ink is needed than that which is used for newspaper or even book printing. The expensive linseed oil is frequently replaced by hemp-seed, poppy, or nut oil. In order to obviate the necessity of boiling the oil down so thick, rosin is sometimes added to the varnish. Thus, to one hundred and twenty parts of linseed oil forty to fifty parts of rosin are added and twelve to fourteen parts of soap. Rosin oil is also used in place of a part of the linseed oil; indeed, cheap printing ink can be made composed of rosin oil, rosin, soap, and lamp-black alone, without the addition of linseed oil at all.

Colored printing inks are obtained by adding to the boiled-oil varnish vermilion, Prussian blue, indigo, and other colors.

4. MANUFACTURE OF OIL-CLOTH, LINOLEUM, ETC.—In the manufacture of oil-cloths, the basis is a coarse canvas, of jute or cotton stuff usually, which is coated with repeated layers of linseed oil, which has been previously boiled sufficiently with litharge, and to which the coloring matter has been added, or, in other words, a linseed-oil paint. Before putting on the coatings of paint, the canvas is primed with a coating of size. The object of this is not only to give a body to the cloth, but also to protect the fibre from the injurious action of the acid products generated during the oxidation of the linseed oil which is subsequently applied. Cloth which is covered with paint without a protective coating of size soon becomes rotten and brittle. Both sides of the canvas are painted in this way. After thorough drying of this layer a second coat is applied to both sides. This suffices for the back of the oil-cloth. The painting of the face side is continued until it is sufficiently built up for the printing of the pattern. Most of the printing is hand-printing done by blocks, the number of which correspond to the number of colors to be used.

*Linoleum* is a name often given to a form of oil-cloth in which powdered cork and pigment are incorporated with a thoroughly oxidized linseed oil. A pattern may then be printed on and a transparent varnish to cover all.

The oxidized oil used in linoleum manufacture has sometimes both rosin and kauri gum added to it to give it toughness. The proportions for ordinary linoleum are: Oxidized oil, eight and one-half hundredweight; rosin, one hundredweight; kauri gum, one-half hundredweight. A variety of linoleum containing wood fibre instead of ground cork has of late years been introduced as a substitute for wall-papering under the name of "lincrusta."

5. PROCESSES OF TREATMENT OF CAOUTCHOUC AND GUTTA-PERCHA. —The crude rubber as brought into commerce is quite impure from accidental causes, and, in many cases, from intentional adulteration. It, therefore, must undergo a thorough mechanical cleaning before being submitted to any chemical treatment. It is first boiled with water (to which a little slaked lime is advantageously added) until thoroughly softened, then cut into slices and passed repeatedly between grooved rollers, known as washing rollers, while a stream of cold water flows over it. This crushes and carries away any solid impurities as well as those which are soluble. Under this treatment Para rubber loses from twelve to fifteen per cent. of its weight; the African variety, twenty-five to thirty-three per cent. After this wash-

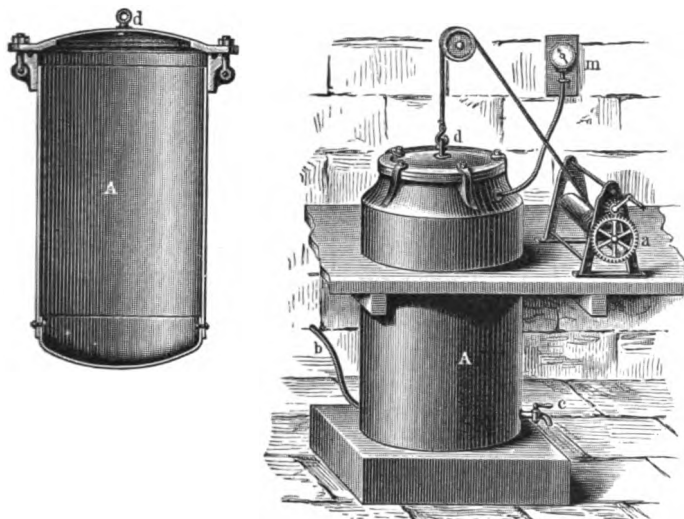
ing, the rubber is carefully and thoroughly dried. Neglect of this frequently causes the wares when subsequently vulcanized to appear spongy. The caoutchouc is now to be worked over and agglomerated thoroughly, which is done either by passing it repeatedly between rollers heated to 70° or 80° C., or by the aid of the so-called masticating or kneading machine, which consists of a hollow cylinder within which revolves another cylinder with a fluted or corrugated surface. The rubber being placed in the annular space between the two cylinders, the inner one is made to revolve, whereby the mass is worked over and over and thoroughly kneaded. The rubber is now to be mixed with the sulphur needed for its vulcanization and with whatever coloring or weighting materials are to be used. This mixing is effected by the aid of horizontal rollers heated internally with steam, and so geared as to move in contrary directions at unequal speed. This mixed rubber so obtained can readily be softened by heat, and can now be shaped, moulded, or rolled into any desired shape, and then submitted to the heat necessary for vulcanization.

The vulcanization of rubber consists in effecting a combination of the caoutchouc with sulphur or sulphides whereby the behavior of the caoutchouc towards heat and towards solvents is changed. Its value for technical purposes is greatly increased by this change.

Two methods of vulcanization are to be noted: (1) the vulcanizing by mixing with sulphur or metallic sulphides and heating to 125° to 140° C.; (2) the cold vulcanization process of Alexander Parkes, consisting of immersing the rubber articles in a solution of chloride of sulphur in carbon disulphide or benzene. The latter process is only used for small articles or those consisting of thin layers of caoutchouc, as the action of the chloride of sulphur, even in the two and one-half per cent. solution usually employed, is very rapid, while at the same time it is superficial, so that it is difficult to control the action properly. In vulcanizing by the first process, that of "burning," as it is termed, the crude caoutchouc is mixed with varying amounts of sulphur; for soft rubber goods with about ten per cent., for hard rubber or vulcanite with thirty to thirty-five per cent., of sulphur. Instead of sulphur, metallic sulphides are used, such as alkaline sulphides, sulphide of lead, and sulphide of antimony. For red rubber goods the latter is always used. For soft rubber articles the proper temperature for vulcanization lies between 120° and 136° C.; for hard rubber, from 140° to 142° C. In vulcanizing, only a part of the sulphur is chemically combined, a part remaining mechanically mixed. This can be largely removed by boiling the finished articles in a solution of caustic soda. Both air-baths and steam-baths are in use for heating, the latter at present in the majority of cases. A form of vulcanizing vessel for smaller articles is shown in Fig. 37. The lid can be removed by the mechanism shown at *a*, and the manometer *m* shows the pressure existing in the vulcanizer *A*. This final heating which effects the change in the rubber is frequently called the "curing" of the rubber. Vulcanized rubber goods can be manufactured in the greatest variety of shapes and for a multitude of uses, the rubber being in almost all cases "cured" after the shaping.

In the manufacture of hard-rubber articles, the East Indian, and specially the Java and Borneo, caoutchouc is used, the Para rubber being too expensive, and besides not so well adapted. While in the manufacture of soft rubber, the burning or curing was the last process, following the shaping of the articles, in the manufacture of the hard rubber the curing is

generally done before the articles are finally shaped. Only in the manufacture of moulded goods is the curing done last. Gutta-percha, balata, and colophony resin are often added to modify the hardness and elasticity, while a large number of mineral substances, such as chalk, gypsum, calcined magnesia, zinc oxide, asphalt, etc., are added chiefly for cheapening purposes.

Fig. 37.

A kind of vulcanite or hard rubber which contains a very large proportion of vermilion is used, under the name of dental rubber, for making artificial gums.

The working over of scrap rubber has in recent years assumed much importance. Although scraps of raw caoutchouc can easily be kneaded or rolled together, vulcanized rubber cannot be. The insolubility of the vulcanized rubber in ordinary solvents presents another difficulty. Although the problem is not yet solved, numerous proposals have been made. These all involve one of three lines of treatment: (1) mechanical subdivision of the scrap and the adding of the powder so obtained to fresh caoutchouc; (2) heating the vulcanized scrap to fusion and use of the pitchy mass so obtained as mixing material; (3) partial desulphurization of the caoutchouc, solution in suitable solvents, driving off the solvent, and use of the residuum so obtained.

*Treatment of Gutta-percha.*—This is quite similar to that described under caoutchouc. The crude gutta-percha must be thoroughly washed and freed from dirt and mechanically mixed impurities. It is then cut or torn into fine shreds, which are, after washing, heated so as to ball them together. It is now kneaded and compacted so as to drive out the air-bubbles.

Gutta-percha is used both in the vulcanized and unvulcanized condition. The vulcanization is carried out, as in the case of caoutchouc, by the addition of sulphur and curing. The amount of sulphur varies from six to ten per cent., and the temperature for vulcanization lies between 135° and

150° C. The gutta-percha scraps are worked up generally by desulphurizing the vulcanized material by boiling for five to six hours in a six to eight per cent. solution of caustic soda, washing, drying, dissolving in carbon disulphide, benzene, or turpentine, and then distilling off the solvent.

## III. Products.

1. PERFUMES.—The general character of the several classes of perfumes has already been indicated in the previous section, while the products are so extremely numerous and special in character that any attempt at detailed description would be beyond the province of this work.

2. VARNISHES.—We have to note here both the natural varnishes, already referred to (see p. 100), and manufactured varnishes. The classification of manufactured varnishes, already given, was: (1) Linseed-oil varnishes, including both plain boiled linseed-oil varnish and solutions of resins in the boiled oil, or lacquers, as they are often called; (2) spirit varnishes, including not only alcoholic solutions of resins, but solutions of the latter in benzol, petroleum spirit, wood-naphtha, and other volatile liquids, and (3) turpentine-oil varnishes.

*Natural Varnishes.*—With regard to the Burmese and Indian lacquers, little is known except as to their production as crude materials. The Japanese lacquer has been more fully described, and the methods of applying it attentively followed. As the varnish flows from the incisions in the trees of the *Rhus* species it is a milky juice, which, on exposure, quickly darkens and blackens in color. After resting in tubs for some time the juice becomes thick and viscous, the thicker portions settle at the bottom of the vessel, and from it the thinner top stratum is separated by decanting. Both qualities are strained to free them from impurities, and when ready for use they have a rich brown-black color, which, however, in thin layers presents a yellow, transparent aspect. This varnish, when applied to any object, becomes exceedingly hard and unalterable, and with it as a basis all the colored lacquers of Japan are prepared. The black variety of the lacquer is prepared by stirring the crude varnish for a day or two in the open air, by which it becomes a deep brownish-black. Towards the completion of the process, a quantity of highly ferruginous water, or of an infusion of gall-nuts darkened with iron, is mixed with the varnish, and the stirring and exposure are continued till the added water has entirely evaporated, leaving a rich jet-black varnish of proper consistency. In preparing the fine qualities of Japanese lacquer, the material receives numerous coats, and between each coating the surface is carefully ground and smoothed. The final coating is highly polished by rubbing, and the manner in which such lacquered work is finished and ornamented presents endless variations. The durability of Japanese lacquer-work is such that it can be used for vessels to contain hot tea and other food, and it is even unaffected by highly-heated spirituous liquors.

*Linseed-oil Varnishes.*—The method of burning linseed or similar drying oil in order to develop its varnish-forming character has been described (see p. 102). The use of metallic oxides and salts as driers has also been referred to. In this connection an additional word may be had. While litharge and lead acetate are commonly used, they must be replaced by manganese or other driers when the boiled oil is to be used as the basis of zinc

oxide paint. Lately, manganous borate has been strongly recommended as a drier, and it is asserted that it is capable of giving rapid drying qualities to linseed oil when it is heated a sufficient length of time (from ten to fourteen days) at a temperature of only 40° C. Such a boiled oil would, of course, be lighter in color than if treated at a higher temperature. Liquid driers are also in use at present which have the advantage of acting gradually upon the linseed oil without the aid of heat, so that a boiled oil of very light color is obtainable. These driers contain manganese and lead linoleates and resinates, and concentrated solutions in oil or turpentine are prepared for addition to the oil to be oxidized. Boiled oil is often bleached by sunlight, and always improves by keeping, as impurities gradually settle out, and its drying qualities develop by age.

The most important of the linseed-oil resin varnishes are: Amber varnish, the most durable and resisting oil varnish, but unfortunately of dark color; copal varnish, the finest of all the oil varnishes, nearly as hard and durable as amber varnish, much paler in color, and drying more quickly; and kauri resin and colophony resin for inferior varnishes. The best oil varnishes are made from "fused" copal or amber, with boiled linseed oil, subsequently thinned out with oil of turpentine.

*Spirit varnishes* are easily obtained perfectly clear; they dry very rapidly, and leave smooth, lustrous films, which appear at first unexceptionable. But slight vibrations and changes of temperature soon develop innumerable small cracks, in consequence of which it loses its lustre, and if the varnish layer was thick it begins to peel off. The reason of this is that the film consisted simply of unaltered resin, spread in a thin layer, and as most of the resins are brittle by nature, slight shocks or changes of temperature, inducing contraction or expansion of the article varnished, will cause the resin film to break. What is true of alcoholic varnishes applies, of course, also to all varnishes where the solvent of the resin takes no part in the formation of the film. The more volatile the solvent the quicker the film is deposited and the easier it cracks. Two methods of obviating this difficulty are in use: first, to mix with the brittle resin a soft, balsam-like resin, and, second, to mix spirit varnish with one prepared with turpentine oil.

*Turpentine varnishes* are seldom used exclusively as such because of the strong and persistent turpentine odor. When used alone they give films as perfect as those gotten by the use of spirit varnishes, but tougher and drying more slowly than these latter. Usually, however, turpentine oil is used in connection with boiled linseed or other drying oil in varnish manufacture, as in the case given of copal varnish, before described (see p. 104). The resins used for turpentine-oil varnishes are the varieties of copal, amber, sandarach, dammar, mastic, and coniferous resins.

*Japans* are simply varnishes that yield, on drying, very hard, brilliant coatings upon paper, wood, or metal, analogous to the natural lacquer of Japan, before described. The effecting of this result is gotten in general by exposing the articles to high temperatures in stoves or hot chambers subsequent to the application of the varnish. This supplementary heating process is called "japanning." It is done with clear, transparent varnishes, in black and in colors, but black japan is the most characteristic and common style of work. Black japan varnish contains asphaltum as the basis, and when applied in several layers, each of which is separately dried in the stove at a heat rising to 300° F. (149° C.), is susceptible of a high polish.

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Japanning may be regarded as a process intermediate between ordinary painting and enamelling. It is very extensively applied in the finishing of ordinary hardware goods and domestic iron-work, deed-boxes, clock-dials, and papier-mâché articles. The process is also applied to blocks of slate for making imitation of black and other marbles for chimney-pieces, etc., and a modified form of japanning is employed for prepared enamel, japan, or patent leather.

3. PRINTING INKS.—The character of printing inks has been sufficiently indicated in the description of its manufacture. (See p. 104.)

4. MISCELLANEOUS PRODUCTS FROM RESINS AND ESSENTIAL OILS.—(1) *Sealing-wax* is a valuable product of manufacture from shellac. Venice turpentine is always added to the shellac to make it more fusible and less brittle, and some mineral coloring matter, which, in the case of the common red variety, is always vermilion. For black sealing-wax the best ivory-black is used, for golden-colored wax, "mosaic gold" (stannic sulphide), for green wax, powdered verdigris. For the commoner varieties, earthy materials, like chalk, magnesia, burnt plaster, barytes, or infusorial earth, are added for the double purpose of making it less fusible and to weight it. Perfumed sealing-waxes are scented with benzoin, Peru and Tolu balsams, and storax. As a substitute for, or adulterant of, shellac in the manufacture of sealing-wax, gum acaroides has recently come into use.

(2) *Rosin Oil.*—In recent years great importance has attached to the products of the dry distillation of common colophony resin or "rosin." It yields, on distillation, two valuable products: first, from three to seven per cent. of a light fraction known as rosin spirit, or "pinoline," and, second, from seventy to eighty-five per cent. of rosin oil, a violet-blue fluorescing liquid, varying in specific gravity from .98 to 1.1. The pinoline is used as an illuminant and as a substitute for turpentine oil in varnish manufacture. The rosin oil has a large use as a lubricant, especially for machinery and wagon-wheels. It is used in the condition of "rosin grease" (made by stirring rosin oil with milk of lime), and largely as a substitute for linseed oil in the manufacture of printer's ink. (See p. 104.) Moreover, as it can be deprived of its fluorescence or "bloom" in various ways (exposure to sunlight, treatment with hydrogen peroxide, nitro-benzene, dinitro-naphthalene, etc.), it can be used in adulterating olive, rape, and sperm oils. The best mineral lubricating oils are also adulterated with it at times.

(3) *Oil-cloth and Linoleum.*—The general outlines of the manufacture of these products as given on page 105, allow one to form an idea of the character of them.

Oil-cloth is a firm but flexible fabric, which by its treatment has been made water-proof and impervious to atmospheric influences. It can be washed and cleansed, and, under ordinary wear, retains for a considerable time its lustre and brilliancy of printed pattern. It is, however, cold and hard, and, unless well seasoned, the pattern is liable to wear off. The covering film will not stand much bending without cracking, and then it rapidly disintegrates.

Linoleum is softer and more elastic to the feet, and, if the composition has been properly made, shows great elasticity and toughness, so that its wearing powers are notably greater than those of oil-cloth. In laying down linoleum, the edges may be cemented to the floor by using a thick solution of shellac in methylated spirit.

(4) *Linseed-oil Caoutchouc.*—For the preparation of this substitute for caoutchouc, linseed oil is heated to a high temperature for a considerable time until it becomes dark and has changed into a tough mass. It is stated that when vulcanized by the acid of sulphur chloride it can be used as a substitute or adulterant of genuine caoutchouc.

5. INDIA-RUBBER AND GUTTA-PERCHA PRODUCTS.—In noting the properties of crude caoutchouc it was stated that the raw caoutchouc, while elastic at ordinary temperatures, did not show the same character when chilled, as it became hard, and when heated it lost the elastic feature entirely. On the other hand, vulcanized caoutchouc or manufactured rubber shows no change in its elasticity, even within very wide limits of temperature. Freshly-cut surfaces, on being pressed together, will not adhere as was the case with raw caoutchouc; it swells up only slightly in bisulphide of carbon, oil of turpentine, and other solvents, while the raw caoutchouc swells up greatly and even dissolves in part. The vulcanized rubber is much more impervious to water than the raw material. As stated before, not all of the sulphur present in the vulcanized rubber is chemically combined. A large excess of uncombined sulphur is, however, deleterious to the goods, as it causes them to lose their elasticity when they are stored for a few years. If such goods are treated with alkaline solutions, the free sulphur can be removed without impairing the elastic character of the vulcanized caoutchouc. Hard rubber, prepared, as described before, from crude caoutchouc, with a larger percentage of sulphur, has a black color and takes a high degree of polish. Articles of this material can also be gotten of any desired color, as in the case of the dental rubber previously referred to. Resins, like shellac, are often added to give elasticity to the hard rubber, the amount of resin capable of being taken up being considerable, equalling at times fifty per cent. of the combined weight of the caoutchouc and sulphur. Hard rubber becomes strongly electrified by rubbing, and hence is used in various plate electrical machines, while its non-conducting qualities make it valuable for insulators in various forms of telegraphic apparatus. Hard rubber is unacted upon by strong mineral acids and other chemicals, and hence is used for acid-pumps and connections, for spatulas, photographic dishes, etc.

*Rubber substitute*, or so-called "artificial rubber," is made by acting upon linseed, rape, poppy, hemp, and cotton-seed oils with sulphur chloride, and removing the hydrogen chloride formed by after-treatment with milk of lime. The result is a tough rubber-like mass, which, however, becomes more or less brittle on keeping.

It is asserted that a better product is obtained by using oxidized or "blown" oils for the treatment with the sulphur chloride. The acid "sludge" from the refining of petroleum is also converted into a rubber substitute by heating and removal of the free acid.

*Gutta-percha*, in the pure as well as the vulcanized condition, has been adapted to a multitude of uses. One of the most important uses of gutta-percha is as a material for the matrices or moulds for coins, medals, smaller art castings, etc., and all forms of galvano-plastic work. The pure gutta-percha serves very well to take imprints, but for overlaying matrices or moulds compositions of gutta-percha and caoutchouc must be used, to unite plasticity when heated with sufficient elasticity to allow of the matrix being removed without injury to the impression. The chief use for gutta-percha, however, is for telegraphic cable insulation (every nautical mile of cable re-

quiring about one-half of a ton of gutta-percha), and the chief purchaser and worker in gutta-percha, therefore, is the "Telegraph Construction and Maintenance Company," of London, who buy up the crude gutta-percha through their agents in Singapore. The gutta-percha is covered upon the wires by pressing. The partly vulcanized and warm gutta-percha mass is forced out of a powerful press along with and around the wire or wires to be covered. The gutta-percha must have previously been well kneaded to remove the air thoroughly from it, so that it may pack uniformly.

Gutta-percha is also incorporated with powdered wood and sawdust, making a composition which is very hard and can be worked by means of the saw and turning-lathe into a variety of shapes.

## IV. Analytical Tests and Methods.

1. For Essential Oils.—Essential oils are extremely liable to adulteration, the high price of many of the finer ones lending to this tendency. The usual adulterations are with alcohol, chloroform, oil of turpentine, fixed oils, both vegetable and mineral, and spermaceti, and by mixing the cheaper essential oils with the more expensive. In addition to the above intentional adulterants, volatile oils are apt to contain water and resinous and other oxygenated bodies, produced by their exposure to air.

The detection of fatty oils, resins, or spermaceti can often be effected by simply placing a drop of a suspected oil upon a piece of white paper and exposing it for a short time to heat. If the oil is pure it will entirely evaporate; but if one of these adulterants be present, a greasy or translucent stain will be left on the paper. These substances will also remain undissolved when the oil is agitated with thrice its volume of rectified spirit.

Alcohol in essential oils may be detected by agitating the oil with small pieces of dry calcium chloride. These remain unaltered in a pure essential oil, but dissolve in one containing alcohol, and the resulting solution separates, forming a distinct stratum at the bottom of the vessel. When only a very little alcohol is present, the pieces merely change their form and exhibit the action of the solvent on their angles or edges, which become more or less obtuse or rounded. If the experiment be performed in a graduated tube and a known measure of the oil employed, the diminution in its volume will give that of the alcohol mixed with it. Dragendorff recommends the use of metallic sodium, which does not act on hydrocarbons, and but slightly in the cold on oxygenated essential oils if pure and dry, but in the presence of ten or even five per cent. of alcohol a small piece of the sodium is dissolved, while a brisk evolution of gas takes place. Aniline-red (magenta) is insoluble in essential oils if pure and dry, but in the presence of a small proportion of alcohol they acquire a pink or red color. This adulteration with alcohol is said to be very common, as it is a frequent practice of druggists to add a little of the strongest rectified spirit to their essential oils to render them transparent, especially in cold weather. Oil of cassia is a notable example of an oil treated in this way.

The adulteration of essential oils with fixed oils is best distinguished by what is termed "steam distillation." The essential oils all distil over with steam at 100° C., while resinous matters and fixed oils, added as adulterants, will remain in the retort. The adulteration of the finer essential oils with

cheaper essential oils is constantly met with. Thus, the expensive oil of cassia is adulterated with oil of cedarwood; oil of rose with oil of geranium; and oil of geranium with oil of turpentine. Noting the specific gravity carefully where that is characteristic, and noting the odor on evaporating, are methods most generally resorted to for the detection of these fraudulent admixtures. The adulteration of essential oils with oil of turpentine is, unfortunately, one of those difficult of detection, and no method of testing has as yet been suggested that will always show it.

The determination of the saponification equivalent has been shown to be of importance in such oils as contain esters, like bornyl acetate, etc. As some oils contain free alcohols, the determination of the acetyl figure is also of importance as a test for purity. Benedikt and Griessner also recommend the determination of the methyl figure in such cases as the analysis of oil of cloves, anise, or fennel.

The essential oils give a variety of color-tests with such reagents as concentrated sulphuric acid, fuming nitric acid, bromine, picric acid, etc., which, however, are not sufficiently characteristic to allow of their being used to recognize adulterations. The purity of oil of turpentine, as commercially the most important of the essential oils, is often a question to be determined. The most usual adulterants of oil of turpentine are light petroleum-naphtha, known as "turpentine substitute," "rosin spirit," and of late a so-called "light camphor oil," gotten as a side-product in the manufacture of safrol. The following tabular statement of Allen * shows the characters of oil of turpentine, rosin spirit, and petroleum-naphtha under the influence of different reagents:

| | Turpentine oil. | Rosin spirit. | Petroleum-naphtha. |
|---|---|---|---|
| 1. Optical activity . . . | Active. | Usually none. | None. |
| 2. Specific gravity . . . | .860 to .872. | .856 to .880. | .700 to .740. |
| 3. Temperature of distillation, C. °. | 156° to 180°. | Gradual rise. | Gradual rise. |
| 4. Action in the cold on coal-tar pitch. | Readily dissolves pitch to a deep-brown solution. | Readily dissolves pitch to a deep-brown solution. | Very slight action, little or no color. |
| 5. Behavior with absolute phenol, 3 of sample to 1 of phenol, at 20° C. | Homogeneous mixture. | Homogeneous mixture. | No apparent solution. |
| 6. Behavior on shaking 3 parts of cold sample with 1 part castor oil. | Homogeneous mixture. | Homogeneous mixture. | Liquid separates into two layers of nearly equal volume. |
| 7. Bromine absorption. | 203 to 236. | 184 to 203. | 10 to 20. |
| 8. Behavior with sulphuric acid. | Almost completely polymerized. | Polymerized. | Very little action. |

It will be seen that the presence of petroleum spirit can be indicated by almost all of these reagents, while that of rosin spirit would hardly be shown. H. E. Armstrong † recommends a process which consists of agitating the suspected turpentine sample first with sulphuric acid and water (2:1), carefully avoiding too high a rise of temperature. This gradually polymerizes the genuine oil of turpentine, changing it to a viscid non-volatile oil. The sample is then distilled with steam, and that which is volatile at this temperature is now treated with 4:1 sulphuric acid and water. The polymerization of the turpentine is usually completed by this

* Allen, Commercial Org. Anal., 2d ed., ii. p. 439.
† Journ. Soc. Chem. Ind., i. p. 480.

treatment, while any petroleum-naphtha present is not affected, and remains as volatile as before. A final steam distillation will give the petroleum-naphtha originally present in the turpentine sample. Rosin spirit is partly polymerized in this treatment, while volatile hydro-carbons remain, but its presence is much harder to indicate certainly than that of petroleum.

Dunwoody has shown that mixtures of turpentine and petroleum are much less soluble in ninety-nine per cent. acetic acid than pure turpentine. While ten cubic centimetres of pure turpentine are soluble in an equal volume of a mixture of ninety-nine parts glacial acetic acid and one part water, it requires forty cubic centimetres of such mixture when the turpentine contains ten per cent. of petroleum, sixty cubic centimetres if twenty per cent. of petroleum be present, and so on in increasing rates.

The Prussian custom regulations prescribe a similar test with aniline oil. Ten cubic centimetres of the sample are shaken up in a stoppered jar with ten cubic centimetres of aniline oil. If pure turpentine is used, a clear solution follows; if petroleum is present, two layers are formed.

The oxidizing effect of fuming nitric acid is also availed of to detect the presence of mineral oil in turpentine, as the latter is entirely oxidized, while the former is not affected. It is stated that this test is perfectly accurate with the higher boiling fractions of petroleum, but that the lighter fractions are slightly attacked.

The bromine absorption of oil of turpentine (see p. 81) is higher than that of any of these adulterants, and that may in many cases serve to indicate its purity.

The iodine absorption percentages with Hübl's reagent (see p. 82) for a large number of essential oils have been determined by R. H. Davies,* who finds that the differences in absorption power are very much greater in the case of essential than in that of fixed oils. Some volatile oils do not absorb any appreciable amount of iodine, while others will remove from solution four times their weight, or four hundred per cent. Thus, oil of turpentine shows an absorption equivalent of three hundred and seventy-seven per cent.

2. For Resins.—The tests for resins or resin acids, when admixed with fats or fatty oils, have been referred to under the discussion of the latter. (See p. 83.)

From admixture with the neutral fixed oils resins may be separated by treating the mixture with alcohol of about .85 specific gravity. The alcohol is subsequently separated, and the dissolved resin recovered by evaporating it to dryness. Acid resins, such as common colophony, may be separated from the neutral fats by boiling the substance with a strong solution of sodium bicarbonate or borax. After cooling, the aqueous liquid is separated from the oil and the resin precipitated from its solution in the sodium salt by adding hydrochloric acid.

Resins may be separated from the essential oils and camphors in admixture with which they so frequently occur by distilling in a current of steam.

The resins show some considerable differences when examined by the two methods of bromine absorption and saponification equivalent, before referred ... der the fatty oils. (See p. 81.) Mills and Muter † have determined ... ine absorptions, and E. J. Mills ‡ the proportions of potash neu-

* ...rn. and Trans., April, 1889, p. 821, and Amer. Journ. of Phar., 1889, p. 301.
† ...oc. Chem. Ind., iv. p. 97. ‡ Ibid., v. 221.

tralized by various resins. The following table gives a summary of their results:

| KIND OF RESIN. | KOH neutralized per cent. | Saponification equivalent. | Bromine absorption. | Hydrobromic acid formed. |
|---|---|---|---|---|
| Rosin (refined) . . . . | 18.1 | 308.6 | 112.7 | . . . |
| Shellac . . . . . . . . | 23.0 | 242.7 | 5.2 | . . . |
| Shellac (bleached) . . | 18.2 | 306.9 | 4.6 | . . . |
| Benzöin . . . . . . . | 22.3 | 256.0 | 38.9 | Some. |
| Amber . . . . . . . . | 16.1 | 347.6 | 53.5 | Some. |
| Animé . . . . . . . . | 9.5 | 585.5 | 60.2 | Much. |
| Gamboge . . . . . . | 15.5 | 361.1 | 71.6 | Much. |
| Copal . . . . . . . . | 12.4 | 450.8 | 89.9 | Much. |
| Copal (reduced to ⅔ by boiling) . . . . . . | 12.9 | 433.4 | 84.5 | Much. |
| Sandarach . . . . . . | 16.4 | 340.6 | 96.4 | Very much. |
| Kauri . . . . . . . . | 12.9 | 433.4 | 108.2 | . . . |
| Thus . . . . . . . . | 21.0 | 340.6 | 108.5 | . . . |
| Dammar . . . . . . . | 5.2 | 1068.1 | 117.9 | Much. |
| Elemi . . . . . . . . | 3.3 | 1697.9 | 122.2 | Very much. |
| Mastic . . . . . . . . | 11.7 | 478.6 | 124.3 | Much. |

The chief feature attracting attention is the low bromine-absorption figure gotten with shellac. Mills's method could probably be used to advantage for the analysis of varnishes after evaporating off the volatile solvent.

Hirschsohn * has elaborated a systematic scheme for the identification of resins, gum-resins, and balsams analogous to the schemes for plant analysis, in which he uses a succession of solvents and reagents. It is too lengthy to be given here in detail. The constantly-widening use of rosin oil makes the tests for its presence of considerable importance. Rosin oil gives a characteristic violet color, with anhydrous stannic chloride or bromide. If it is mixed with fatty oils, A. H. Allen points out that the test may still be successfully applied by distilling the mixture and applying the test to the first fraction which passes over.

Demski and Morawski † recommend the use of acetone for the detection and rough determination of rosin oil in mineral oils. According to these chemists, rosin oils are miscible with acetone in all proportions, while mineral oils require several times their volume of acetone to effect solution. The test is applied by agitating fifty cubic centimetres of the sample with twenty-five cubic centimetres of acetone. If, on allowing the mixture to stand, it separates into two layers, ten cubic centimetres of the upper or acetonic layer should be removed with a pipette and evaporated, and the residual oil weighed. In the case of pure American or Galician lubricating oil the residue will weigh about two grammes, but only half this quantity will be obtained from Wallachian or Caucasian oil. It is stated that mixtures of rosin oil with the lubricating oils from American and Galician petroleum are permanently soluble in half their volume of acetone, if the proportion of rosin oil exceeds thirty-five per cent. of the mixed oil, but that complete solution is not effected in the case of Wallachian and Caucasian oils unless the rosin oil constitutes at least fifty per cent. of the mixture. Ragosine cylinder oil requires an addition of rosin oil equal to fifty-three per cent. of the mixture to become soluble in half its volume of acetone.

* Watts's Dict. of Chem., viii. p. 1743.
† Ding. Polytech. Journ., cclviii. p. 82.

3. For Varnishes.—The most important constituent which enters into the manufacture of varnishes is undoubtedly the linseed or other drying oil. Linseed oil (see p. 49) is liable to be adulterated with other vegetable oils, with fish oils, with mineral and rosin oils, and with rosin itself. As mineral and foreign seed oils are lighter in specific gravity than linseed oil, while rosin and rosin oil are much heavier, by the judicious use of a suitable mixture of mineral and rosin oils extensive adulteration can be effected without alteration of the density. The analysis of a linseed oil supposed to be adulterated would be made according to the scheme given before (see p. 84) for the analysis of a fatty oil containing foreign admixtures. A. H. Allen gives also a rather elaborate method. which he states is better adapted for a boiled linseed oil, for the details of which the reader is referred to Allen's "Commercial Organic Analysis," 3d ed., vol. ii., Part ii., p. 155.

4. For Caoutchouc and Gutta-percha.—The adulterations of caoutchouc are both mineral, or inorganic, and organic in character. A careful incineration of a given specimen in a porcelain crucible will leave any mineral admixture, as ash. Oxide of zinc, gypsum, and such admixtures are thus recognized. To determine the amount of sulphur, the specimen is burned in a current of oxygen, the gaseous products of combustion passed through water acidulated with nitric acid, so that the sulphurous acid retained is changed into sulphuric acid, which is then determined by chloride of barium in the usual way. If the mass contain metallic sulphide, this procedure does not answer. The mass must be deflagrated in a crucible with saltpetre and acid, then the sulphur determined in the sulphate of potassium produced.

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## STATISTICS.

No attempt will be made to take up the essential oils in detail. The statistics of the entire class will be given, and only a few of the more important substances will be specially mentioned.

*Essential Oils.*—The export of essential oils (bergamot, lemon, etc.) from Sicily and Calabria in recent years has been:

| | Kilos. | Value in lire = 0.19$\frac{3}{10}$. |
|---|---|---|
| 1895 | 554,191 | 8,081,870 |
| 1896 | 514,067 | 7,579,424 |
| 1897 | 732,092 | 9,719,133 |
| 1898 | 667,293 | 9,015,083 |
| 1899 | 797,145 | 10,722,445 |

Peppermint oil is exported from Japan in three forms: as dementholized oil, as mixed oil containing about forty per cent. of menthol, and as menthol crystals. The statements of production, therefore, include all three of these sources.

The yield and stock on hand of Japanese peppermint oil in recent years is given as follows by Schimmel & Co.

| | | |
|---|---|---|
| 1896 | 223,300 catties | (298,664 lbs.) |
| 1897 | 140,000 " | (187,250 " ) |
| 1898 | 100,000 " | (133,750 " ) |
| 1899 | 102,000 " | (136,425 " ) |

The American production of peppermint oil for 1897 rose to 251,000 pounds. The production for 1898 continued about the same, but in 1899 it fell to 180,000 pounds.

An estimate of the world's production of peppermint oil in 1899 was 175,000 kilos., of which America furnished 90,000 kilos. and Japan 70,000 kilos.

The exports of cinnamon chips, for the extraction of oil of cinnamon, from Ceylon for the last five years have been:

| Year | Quantity |
|---|---|
| 1895 | 920,136 pounds. |
| 1896 | 808,502 " |
| 1897 | 1,067,051 " |
| 1898 | 1,414,165 pounds. |
| 1899 | 1,829,127 " |

The total exports of chips average about one-half by weight of the total exports of Ceylon cinnamon bark. The world's consumption of bark and chips together during the last few years has been in round numbers 3,500,000 pounds a year.

The exports of citronella oil from Ceylon (Colombo and Galle) have been as follows for the past five years:

| Year | Quantity |
|---|---|
| 1895 | 1,182,255 pounds. |
| 1896 | 1,132,141 " |
| 1897 | 1,182,867 " |
| 1898 | 1,365,917 pounds. |
| 1899 | 1,478,756 " |

The production of spirit of turpentine in the United States amounts at present to about 25,000,000 gallons, of a value of about $8,500,000.

The exportations of turpentine spirit from the United States during the last five years were:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Gallons | 14,652,738 | 17,431,566 | 17,302,823 | 18,351,140 | 17,760,533 |
| Valued at | $3,998,277 | $4,613,811 | $4,447,551 | $5,380,806 | $6,100,419 |

The British importations of turpentine during the same years have been:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Hundredweight | 503,683 | 498,791 | 502,790 | 573,087 | 495,808 |
| Valued at | £520,065 | £490,381 | £516,887 | £652,740 | £809,906 |

Germany and Belgium each import from a quarter to a third as much turpentine spirit as the United Kingdom.

*Cam*[illegible]—The exportations of camphor from Japan during recent years [illegible]llen off considerably. They were for 1897, 1,552,000 pounds, and [illegible], 1,448,000 pounds. Considerable additional quantities are [illegible]n Formosa, besides the Chinese exportation, for which no [illegible]tainable.

[illegible]ntities imported into the United States for the last five years

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| [illegible] | 1,500,739 | 945,629 | 1,469,601 | 2,047,234 | 1,807,889 |
| Va[illegible] | $284,968 | $328,457 | $332,748 | $365,652 | $322,100 |

[illegible]xportations of rosin (colophony resin) from the United [illegible] five years have been as follows:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| [illegible] | 1,862,394 | 2,172,991 | 2,429,116 | 2,206,203 | 2,563,229 |
| [illegible]l at | $3,351,250 | $4,151,748 | $4,688,163 | $3,689,252 | $3,741,581 |

The English importations of rosin for the last three years were: for 1897, 1,640,745 hundredweight, valued at £407,771; for 1898, 1,662,279 hundredweight, valued at £361,169; for 1899, 1,708,630 hundredweight, valued at £399,556.

The importations of shellac for the last five years to the United States have been as follows:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Pounds | 6,401,060 | 6,056,957 | 7,151,459 | 6,984,395 | 9,830,111 |
| Valued at | $1,288,501 | $1,210,802 | $1,082,401 | $939,361 | $1,397,635 |

The English importations during the same period were:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Hundredweight | 114,122 | 157,352 | 177,557 | 96,678 | 108,757 |
| Valued at | £629,459 | £776,117 | £751,099 | £333,326 | £372,585 |

The exportations of kauri (dammar) resin from New Zealand within recent years have been as follows:

| | | |
|---|---|---|
| 1888 | 8,482 tons, valued at | £380,938 |
| 1889 | 7,519 " " " | 329,590 |
| 1890 | 7,438 " " " | 378,563 |
| 1891 | 8,388 " " " | 437,056 |
| 1892 | 8,705 " " " | 517,678 |
| 1893 | 8,317 " " " | 510,775 |

An estimate of the present annual production of caoutchouc throughout the world, which appeared in the *Monthly Bulletin of the Bureau of the American Republics*, is as follows:

| | |
|---|---|
| Brazil and Peru (yield of Pará rubber) | 45,000,000 pounds. |
| Brazil (yield of Ceará rubber) | 9,400,000 " |
| Brazil (yield of Mangabeira rubber) | 6,500,000 " |
| Guiana | 600,000 " |
| Bolivia | 3,000,000 " |
| Rest of South America | 4,000,000 " |
| Total for South America . . . 68,500,000 pounds. | |
| Central America and Mexico | 5,000,000 " |
| Java, Borneo, and Malayan Islands | 2,000,000 " |
| East and West Africa | 48,000,000 " |
| Madagascar and Mauritius | 1,000,000 " |
| India and Burmah | 800,000 " |
| Ceylon | 15,000 " |
| Total world's production | 125,315,000 " |

Of this amount, the United States and Canada use 40,000,000 pounds, Great Britain and colonies (Canada excepted), 45,000,000, and the continent of Europe, 40,000,000 pounds.

*Gutta-percha.*—The entire world's production of gutta-percha in 1890 was estimated at 4,500,000 kilos. This amount has decreased notably since 1890, amounting in 1896 to only 2,600,000 kilos.

The United States importations of crude caoutchouc and gutta-percha for the last five years have been:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Caoutchouc (lbs.) | 39,741,607 | 36,774,460 | 35,574,449 | 46,055,497 | 51,063,066 |
| Valued at | $18,353,121 | $16,603,020 | $17,457,976 | $25,386,010 | $31,707,630 |
| Gutta-percha (lbs.) | 1,326,794 | 3,843,854 | 1,117,665 | 636,477 | 518,939 |
| Valued at | $122,261 | $178,513 | $100,187 | $159,381 | $167,577 |

The English importations of caoutchouc and gutta-percha have been for the same period:

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Caoutchouc (cwt.) . | 341,553 | 431,164 | 396,929 | 489,601 | 449,647 |
| Valued at . . . . | £3,760,178 | £4,993,186 | £4,553,416 | £6,215,183 | £5,925,643 |
| Gutta-percha (cwt.) | 48,077 | 43,805 | 41,442 | 63,222 | 82,487 |
| Valued at . . . . | £389,258 | £401,490 | £400,975 | £676,274 | £1,005,913 |

The German importations of caoutchouc and gutta-percha for the past two years have been:

| 1898. | 1899. |
|---|---|
| 10,097,700 kilos. | 18,916,400 kilos. |
| Valued at 54,528,000 marks. | Valued at 75,149,000 marks. |

The French importations for the same period were:

| 1898. | 1899. |
|---|---|
| 5,812,000 kilos. | 6,128,200 kilos. |
| Valued at 32,722,000 francs. | Valued at 37,750,000 francs. |

# CHAPTER IV.

## THE CANE-SUGAR INDUSTRY.

### I. Raw Materials.

ALTHOUGH sucrose, or cane-sugar, is present in a great many plants, it is usually accompanied by relatively large quantities of other carbohydrates, such as glucose, starch, etc., so that its extraction on a commercial scale is practically impossible. In order to extract the cane-sugar advantageously, glucose, invert sugar, and other dissolved solids must not be present in amount relatively large as compared with the sucrose. If this ratio of sucrose to total dissolved solids, called the "coefficient of purity," falls below a certain percentage (usually put at sixty-five), the plant-juice cannot be economically worked for the extraction of crystallized cane-sugar. At the present time the sucrose is extracted from four different sources, and on what may be termed a commercial scale from two only.

1. THE SUGAR-CANE.—The sugar-cane belongs to the family of grasses, growing, however, to an exceptionally large size. The plant is known as *Saccharum officinarum*, and the best known varieties are called by such names as Bourbon cane, Otaheite purple cane, ribbon cane, crystalline cane, and Java cane. It has a wide range, succeeding in almost all tropical and sub-tropical countries, and requires a warm, moist climate, developing most luxuriantly on islands and sea-coasts in the tropics. It is the richest in sugar of all the plants cultivated for this purpose. Under ordinary favorable conditions it yields about ninety per cent. of juice, which contains eighteen to twenty per cent. of crystallizable cane-sugar. The following analyses of sugar-canes from several sources illustrate its composition:

| | Martinique. (Peligot.) | Guadeloupe. (Dupuy.) | Mauritius. (Icery.) | Martinique. (Popp.) | Middle Egypt. (Popp.) | Upper Egypt. (Popp.) |
|---|---|---|---|---|---|---|
| Water . . | 72.1 | 72.0 | 69.0 | 72.22 | 72.15 | 72.13 |
| Sucrose . . | 18.0 | 17.8 | 20.0 | 17.80 | 16.00 | 18.10 |
| Glucose . | . . | . . | . . . | 0.28 | 2.30 | 0.25 |
| Cellulose . | { 9.9 | 9.8 | 10.0 | 9.30 | 9.20 | 9.10 |
| Salts . . . | { . . | 0.4 | 0.7 to 1.2 | 0.40 | 0.35 | 0.42 |
| | 100.00 | 100.00 | 99.7 to 100.2 | 100.00 | 100.00 | 100.00 |

The most successful cultivation of the sugar-cane is at present carried on in Cuba and other West Indian islands, although largely produced in almost all tropical countries.

2. SUGAR-BEET.—The sugar-beet is a source of sucrose that, while first mentioned as long ago as 1747, when Marggraf called the attention of the Berlin Academy of Sciences to its importance as a sugar-yielding material, has only in the last few decades advanced to great importance and

taken position as a successful rival of the sugar-cane in the matter of production. It has been greatly improved by careful selection and cultivation, and its richness in sugar notably increased. Marggraf could only extract 6.2 per cent. of sugar from the white and 4.5 per cent. from the red beet; it has now been brought to an average of eleven per cent., and in exceptional cases has been found to contain sixteen per cent. Some six varieties are now cultivated in Germany, where the beet-sugar industry has reached its highest development: the white Silesian, the Quedlinburg, the Siberian, the French, the Imperial, and the Electoral. (The beet is relatively much more complex in its chemical composition than the sugar-cane, and the expressed juice contains a number of organic impurities not present in the juice of the cane, notably of the class of nitrogenous or albuminoid substances. On the other hand, glucose, or invert sugar, which is frequently present in the cane, is practically absent in the juice of fresh beets.) The detailed composition of the sugar-beet is seen from the accompanying scheme of Scheibler.* At the same time the three accompanying analyses by R. Hofmann gives the composition of three types of beets: those poor in sugar, those of medium richness, and those containing the largest percentage.

| | First type. | Second type. | Third type. |
|---|---|---|---|
| Water | 89.20 | 83.20 | 75.20 |
| Sugar | 4.00 | 9.42 | 15.00 |
| Nitrogenous compounds | 1.00 | 1.64 | 2.20 |
| Non-nitrogenous compounds { soluble | 4.13 | 3.34 | 4.23 |
| Non-nitrogenous compounds { insoluble (cellulose) | 1.01 | 1.50 | 2.07 |
| Ash | 0.66 | 0.90 | 1.30 |
| | 100.00 | 100.00 | 100.00 |

3. Sorghum Plant.—The sorghum plant (*Sorghum saccharatum* and other species) has been known and valued in China for ages, and small quantities have been cultivated in the United States for the sake of the syrup for a number of years past. It is only of recent years, however, that attention has been drawn to it as a source of crystallized sugar, chiefly by the experiments of the United States Bureau of Agriculture, and its systematic cultivation has been attempted in several parts of the United States. The composition and saccharine strength of the juice seems to be quite variable, and dependent upon conditions of cultivation to a much greater extent than is the case with either the sugar-beet or the sugar-cane. Thus, in 1883 the mean per cent. of sucrose in the sorghum juice, analyzed by the chemists of the department, was 8.65, in 1884 the mean was 14.70 per cent., in 1885 it was 9.23, and in 1886 it was 8.60 per cent. The sorghum plant grows easily over a very wide range of climate, and if its cultivation can be established definitely upon correct principles, it may prove to be a most valuable addition to the world's sugar-producing materials.

4. The Sugar-maple.—The sap of *Acer saccharinum* and other species of the genus *Acer* is a source of sugar and syrup more esteemed for confectionery and table use than because of its commercial importance. The sugar is never refined, and only comes into use as a raw, small-grained

* Bericht über Entwick Chem. Ind., von Hofmann, 1877, 3te Heft, p. 187.

## GENERAL VIEW OF THE COMPOSITION OF THE SUGAR-BEET.

84.5 to 79 per cent. water.

15.5 to 21 per cent. solid substance of the beet.

- 11.5 to 17 per cent. — Substances dissolved in water. — Juice.
  - Water.
  - Sugar $C_{12}H_{22}O_{11}$.
  - Non-sugar. (Solid substance of the juice.)
    - Ash
      - Of incombustible salts. — Potassium, sodium, rubidium, calcium, magnesium, iron, and manganese, combined with chlorine, sulphuric, phosphoric, silicic, and nitric acids.
      - Of salts burning to carbonates. — The same metals combined with oxalic, citric, malic, and other acids.
    - Nitrogenous compounds.
      - Proteids (albumen, etc.).
      - Plasma (protagon).
      - Asparagine, $C_4H_8N_2O_3 + H_2O$, and other amides.
      - Betäine, $C_5H_{11}NO_2 + H_2O$.
    - Non-nitrogenous compounds.
      - Arabic acid (beet-gum), $C_{12}H_{22}O_{11}$.
      - Dextrine, $C_{12}H_{20}O_{10}$.
      - Soluble pectic bodies.
      - Coloring matters (chlorophyll).
      - Colorless compounds taking color in the air. (Chromogens.?)
      - Fats.
      - A substance with biting taste.
      - Etc., etc.
- 4 to 4 per cent. mark. — Cellulose, pectose, plasma, pararabin, and coloring matters; incrusting substances. — Insoluble in water.

100 — 100 per cent.

sugar of peculiar and characteristic flavor; the syrup is a thin, sweet syrup of the same characteristic maple flavor, differing considerably, too, in its composition from both cane- and beet-sugar syrups. The freshly-collected sap contains from two to four per cent. of sucrose, with traces of glucose.

We may now compare the chemical composition of the freshly-expressed juice from the three sources of sugar manufacture above described, and note those differences which are of importance in determining the successful extraction and crystallization of the cane-sugar.

The composition of the fresh juice of the sugar-cane is illustrated in the following table. The first four analyses are by the United States Bureau of Agriculture and were made in connection with its experimental work, and the last six from experimental cultivation of certain varieties of cane in Cuba on the Soledad estate of Mr. E. Atkins.

| | LOUISIANA. | | | | CUBA. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1884. | 1885. | 1886. | 1887. | Crystalline cane. | | Red ribbon cane. | | Black Java cane. | |
| Specific gravity | 1.068 | ... | 1.066 | 1.066 | 11.6° B. | 12.5° B. | 11 2° B. | 12.1° B. | 12.2° B. | 11.8° B. |
| Total solids | 16.54 | 15.80 | 16.20 | 16.37 | 20.9 | 22.6 | 20.2 | 21.9 | 22.0 | 21.4 |
| Sucrose | 13.05 | 12.11 | 13.50 | 18.69 | 19.2 | 20.5 | 18.5 | 20.0 | 21.3 | 20.6 |
| Glucose | 0.67 | 1.02 | 0.61 | 0.77 | 0.66 | 0.20 | 0.14 | 0.31 | Trace. | 0.08 |
| Albuminoids | 0.19 | 0.16 | 0.167 | .... | Non-sugar. 1.04 | Non-sugar. 1.90 | Non-sugar. 1.56 | Non-sugar. 1.69 | Non-sugar. 0.70 | Non-sugar. 0 71 |
| Coefficient of purity | 78.97 | 76.64 | 83.33 | 83.48 | 91.8 | 90 7 | 91.5 | 91.3 | 96.8 | 96.3 |

The average composition of the fresh beet juice is shown in the following analyses, the method of obtaining the juice being also indicated. The first four are from "Stammer's Lehrbuch," and represent each the average of a German beet-sugar factory for the season; the fifth is from beets cultivated at Washington, D. C., by the Bureau of Agriculture; the sixth the average of a week's work at Alvarado, California, in 1888, and the last from a beet grown at Grand Island, Nebraska, and analyzed at the State Agricultural Experiment Station.

| | German. By pressure. | German. By diffusion. | German. By centrifugating. | German. By maceration. | Washington. By pressure. | Alvarado, Cal.* By diffusion. | Grand Island, Neb.† H. H. Nicholson. |
|---|---|---|---|---|---|---|---|
| Total solids (degree Brix.) | 16.27 | 17.20 | 14.99 | 18.77 | 11.78 | 17.20 | 23.70 |
| Sucrose | 13.02 | 14.63 | 11.98 | 14.64 | 7.61 | 14.80 | 21.41 |
| Reducing sugar | ... | ... | ... | ... | 0.39 | ... | 0.138 |
| Non-sugar | 3.25 | 2.57 | 3.01 | 4.13 | 3.78 | 2.4 | 2.152 |
| Coefficient of purity | 80.02 | 85.14 | 79.92 | 77.99 | 64.60 | 85.5 | 90.3 |

The composition of the sorghum juice of different seasons, as cultivated by the United States Department of Agriculture, is shown in the following table:

* Many beets grown near Alvarado in the fall of 1888 polarized twenty per cent., and the average coefficient of purity for the season was estimated to be from eighty-five to eighty-seven per cent.

† Individual beets grown in Nebraska have shown a percentage of 22.08 sucrose, and a coefficient of purity of ninety-three per cent.

| | 1883. | 1884. | 1885. | 1886. | 1887. | |
|---|---|---|---|---|---|---|
| | | | | | Fort Scott. | Rio Grande. |
| Total solids | 18.59 | 19.75 | 15.07 | 17.08 | 16.14 | 14.02 |
| Sucrose | 8.65 | 14.70 | 9.23 | 9.59 | 9.54 | 8.98 |
| Glucose | 4.08 | 1.27 | 3.04 | 4.25 | 3.40 | 3.24 |
| Non-sugar | 0.86 | 3.78 | 2.80 | 3.24 | 3 20 | 1.80 |
| Coefficient of purity | 63.65 | 74.43 | 61.25 | 56.15 | 59.11 | 64.05 |

Analyses of fresh maple-sap made at Lunenburg, Vermont, by one of the chemists of the Department of Agriculture, in the spring of 1885, shows that it contains an average of 3.50 per cent. of sucrose, traces only of glucose, about .01 per cent. of albuminoids, and has a mean coefficient of purity of 95.

## II. Processes of Treatment.

1. PRODUCTION OF SUGAR FROM THE SUGAR-CANE.—As the cultivation of the sugar-cane is chiefly carried on in the tropical countries, parts of which are dependent upon totally unskilled labor, there is very great diversity in the development which the industry has reached. In some countries the work is still done by hand or with the simplest kind of machinery, with corresponding small yield of inferior products, while, in others, as in Louisiana, Demerara, Cuba and other West Indian islands, there are many sugar plantations equipped with the very latest and best of sugar-making machinery, and producing direct from the juice raw sugars that are almost equal to the refined product. In general, however, the sugars produced on the plantation are not in a sufficiently pure condition for consumption and are termed "raw sugars," having therefore to undergo a process of refining, by which the impurities are eliminated and the sucrose obtained in a pure, well-crystallized state. We shall note first the method of producing raw sugar, and afterwards the methods of refining the same at present in use.

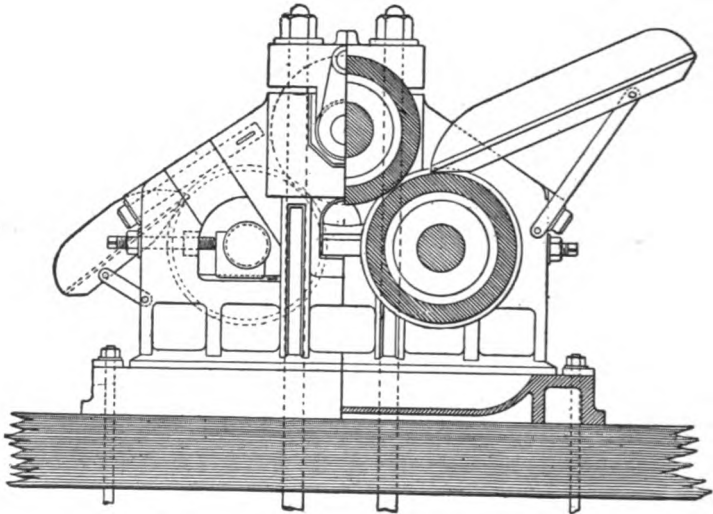
The canes must be cut when they have arrived at maturity, and must be promptly used to prevent the fermentation of the albuminoid constituents and other non-sugar of the cane, which in turn rapidly change sucrose into invert sugar and lessens the possible yield of crystallizable sugar. At least this immediate use of the cut cane is necessary in Cuba, Demerara, and distinctly tropical countries, where the juices must be expressed within forty-eight hours after the cutting to prevent an excessive inversion taking place. In Louisiana, the experiments of the Department of Agriculture have shown * that sound canes can be kept stored under cover for two or three months without appreciable diminution in the sucrose per cent. or loss in the coefficient of purity.

The expression of the juice has been, and in most cases still continues to be, effected by the process of crushing the canes between heavy rolls, which may vary from the crude stone or iron rolls, driven by water or horse-power, to the perfected sugar-mills now in use, in which enormous, hollow, steam-heated rolls, driven by steam, are used to do the same work. Large, slow-moving rolls have been found in practice to yield better results

* Bulletin No. 5, p. 57.

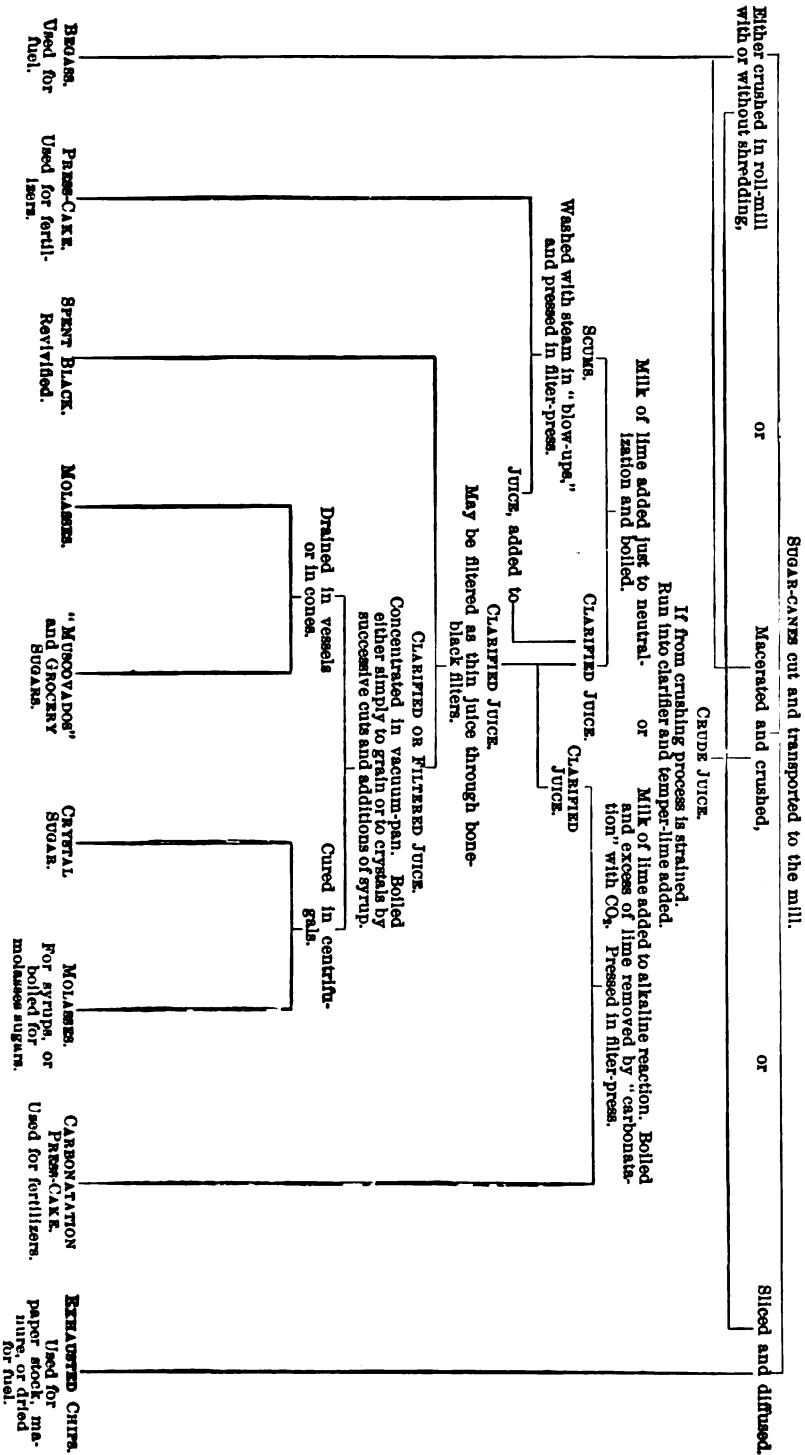
than smaller, rapid-moving rolls. While four, five, and even nine-roll mills have been constructed, the mill in general use is a three-roll mill, an example of which is shown in Fig. 38. The canes pass by the carrier, down the slide, through the rolls, and the "bagasse" (exhausted canes) emerging below is carried away for fuel purposes, while the juice as expressed collects in a receptacle and is run to the evaporators.

While the analyses of sugar-canes, given on a previous page, show that the cane contains ninety per cent. of juice, the percentage of extraction of juice by this roller-crushing process on the best-managed Cuban estates does not exceed seventy or seventy-one, and generally ranges from sixty to sixty-five, per cent. This imperfect liberation of the cane juice by the crushing process has led to experiments in other directions. One result has been the frequent introduction of a second or supplementary crushing of the cane in a two-roll mill following the use of the three-roll mill before

FIG. 38.

described. These second rolls are heavier, and the pressure is greater than in the first crushing. The total percentage of juice, and consequently of sugar extracted from the cane, is raised, although the juice from the second and heavier pressure is less rich in sucrose than the first juice, which came from the softer pulp of the cane.

It has also been sought to increase the yield of saccharine juice by submitting the cane to the action of hot water or steam at an intermediate stage between the two crushings. It is stated that a "maceration" process of this kind, known as Duchassing's, has been in quite successful use in Guadeloupe, raising the yield of sugar from 9.40 per cent. on the cane to 11.04 per cent.

All the processes hitherto described for extracting the juice from the cane have depended for success upon the rupture of the juice-containing cells. "Diffusion," which has been so successful in the extraction of the juice of the sugar-beet, differs from them essentially in dispensing with the breaking up of the cells, and in substituting therefor a displacement by osmosis or diffusion of the saccharine juice by pure water. As a description of this method follows when speaking later of the treatment of the

# GENERAL VIEW OF THE PRODUCTION OF SUGAR FROM THE SUGAR-CANE.

sugar-beet, we will at this stage speak only of the advantages and disadvantages of its application to the sugar-cane work. It has not met at all with general favor from sugar-cane planters. Difficulties were met with in cutting the chips needed for the diffusion-cells. The sugar-cane differs so radically in its structure from the sugar-beet that totally different forms of slicing apparatus had to be used. The cane-chips tended to pack in the cells, and so impeded the circulation of the warm water. When this took place, fermentation and inversion of the sucrose rapidly followed. The cane-chips, after exhaustion, do not make as good a fuel as the bagasse of the cane-mill. The first of these difficulties has been overcome both in the use of diffusion apparatus in Guadeloupe and by the United States Department of Agriculture in its experiments on diffusion, as applied to the sugar-cane made at Fort Scott, Kansas, in 1886. The second difficulty has in part been overcome by using hotter diffusion water (at 90° C.), and working more rapidly with a sufficient pressure. But it is more effectually prevented by the use, in the diffusion-cells, of either carbonate of lime, as proposed and patented by Professor M. Swenson, or of dry-slacked lime, as proposed by Professor H. W. Wiley, the chemist of the Department of Agriculture. Of these, the latter seems to meet with more general approval of those who have tried diffusion with either the sugar-cane or the sorghum-cane. In answer to the third difficulty, it is remarked that the bagasse burns better largely because of the notable quantity of sugar left in it, and that when the diffusion-chips are dried they will burn fairly. They can also be used to great advantage for paper stock and for manure, as they still contain most of the nitrogenous constituents of the cane. On the other hand, if successfully carried out, it undoubtedly effects a more complete extraction of the sugar than any other process. At Monrepos, Guadeloupe, with Bouscaren's apparatus, consisting of six diffusors, juice having a density nearly equal to that of the natural juice is obtained, one and a half hours being sufficient for extracting the sugar. The yield of white sugar amounts to twelve and a half to thirteen per cent. of the weight of the cane.* At Fort Scott, Kansas, the chemists of the Department of Agriculture,† in their experiments with diffusion as applied to sugar-canes, succeeded in obtaining a yield the highest ever got from sugar-cane. The mean loss of sugar in the chips at Fort Scott was .38 per cent., and the quantity of sugar present was 9.56. The percentage of extraction was, therefore, ninety-six per cent., or, reckoned on the weight of cane, 86.4 per cent. of a possible ninety, which, if compared with the best figures obtained in mill-crushing, shows a decided advantage for diffusion.

The treatment of the expressed juice is next to be noted. This has also undergone considerable improvement in recent years, although on small isolated sugar plantations the primitive and wasteful methods of the "copper-wall," or open-pan, boiling are still in use. The general outlines of the treatment of the juice which is followed in the main, if not always in detail, is given in the accompanying scheme.

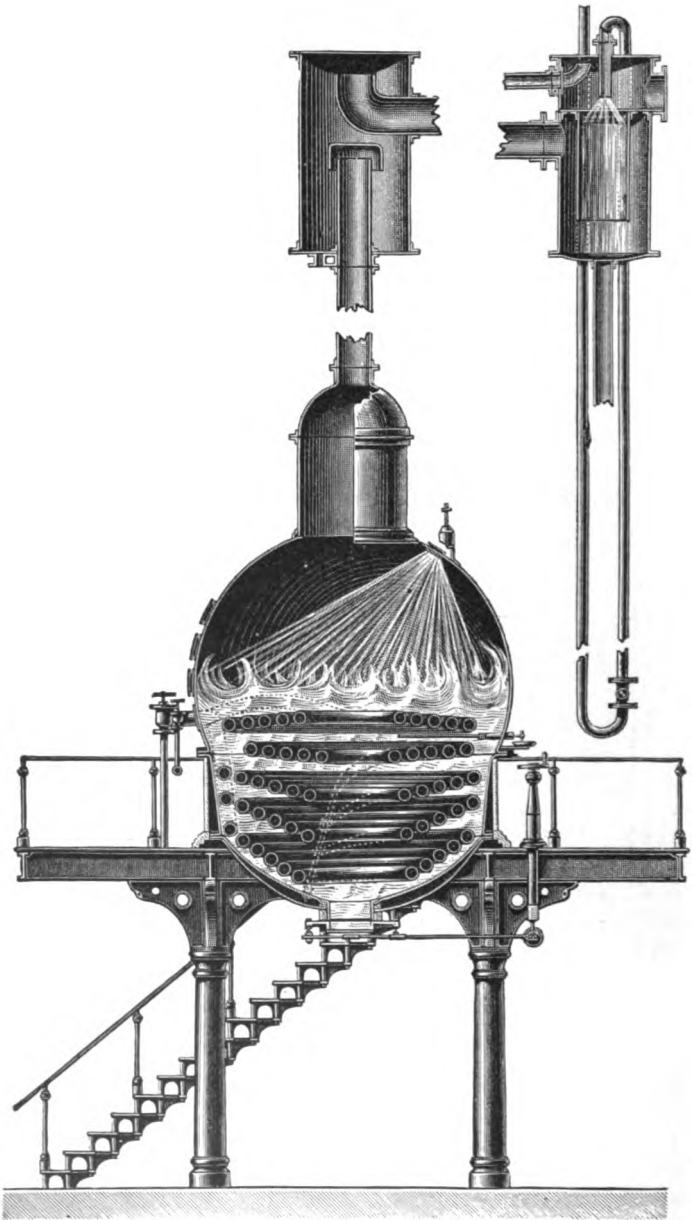
The juice of the sugar-cane must be properly "defecated," or treated with milk of lime, in order to neutralize the organic acids of the juice, and so prevent their starting a fermentation and consequent inversion of the sucrose when the juice is heated. This has the effect, as soon as the juice is heated, of bringing to the surface a thick scum of lime salts, holding

* Spon's Encyclopedia, p. 1881. † Bulletin No. 14, p. 53.

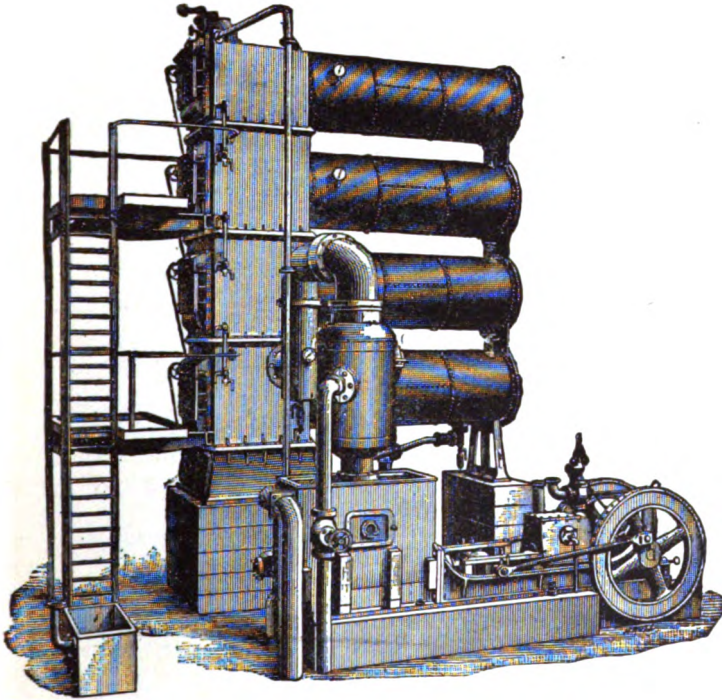
mechanically entangled much of the albuminoids and suspended particles of fibre of the juice. This is known as the "blanket-scum." This is removed by skimming, and the boiling continued, when additional greenish scum forms, which is similarly removed. When the scum ceases to form, the steam is shut off and the sediment allowed to settle, and the clarified juice gradually drawn off. The amount of lime to be added in the case of cane juice is usually .2 to .3 per cent., or about four ounces of quicklime to the gallon of juice, but is always carefully controlled, so that the acids of the juice are not entirely neutralized and a faint acid reaction still remains. Should the lime be in excess, the glucose almost always present in the cane juice is rapidly acted upon and decomposed, yielding dark-colored products. An excess of lime is always corrected before further treatment by the addition of sulphurous, sulphuric, or phosphoric acids. In the older process of open-pan boiling, this defecating and clarifying takes place in the first of five connected kettles or pans, walled in and heated by the same fire, and known technically as the "copper-wall." From this first pan the juice, after the removal of the blanket-scum, goes to the second, in which it receives more heat. After it is thoroughly clarified and both scum and sediment removed, the juice goes to the third and fourth pans successively, in which it is concentrated to 30° B., and then goes to the fifth, or "strike-pan," to be brought to the crystallizing point. It may still require some treatment here, as it first becomes thick. If "sticky" or sour, some buckets of lime-water are let in, or if too dark-colored, dilute sulphuric acid is added to clear it. When the "masse-cuite," or thick mass, full of separating crystals, has been sufficiently heated, it is "struck out" into large, shallow, crystallizing vessels and allowed to cool, and so complete the crystallization. The older open-pan sugars are generally "cured," or freed from syrup, simply by draining in vessels with perforated bottoms, or, in a limited number of cases, by the process of "claying," or covering the sugar in cones with a batter of clay and water, through which water percolates, slowly displacing the darker syrup. The first method gives the common "muscovado" sugar, a moist, brown sugar, which goes from the West Indies to the United States and Europe for refining; the second method gives a lighter-colored but soft-grained sugar, which similarly must be refined for use. This older and cruder method has given place most generally now to improved methods, whereby the yield is notably increased and grades of raw sugars are produced that are much purer and finer in appearance. The chief improvements consist in the use of vacuum-pans for concentration of the juice and centrifugals for curing the crystallized sugar. At the same time other minor improvements contribute no little to the better results. The juice, unless it has been gotten by diffusion, is generally run through a strainer into the clarifier. In addition to very careful and exact measuring of the amount of "temper-lime" needed, sulphurous acid or sulphites are often used now to bleach the juice. In case sulphurous acid is used, more lime is needed for tempering. The thin clarified juice is then filtered through bone-black filters before it goes to the vacuum-pan. This filtration removes the vegetable coloring matters as well as the finely suspended impurities that remain.

The use of powdered lignite as a means of clarifying and improving the raw-sugar juices, first introduced by Kleeman, has been tried in recent years, and, it is claimed, with success and profit. It is added after the juice has been limed and defecated, and the juice, together with the accumulated

skimmings and bottoms and the lignite, are thoroughly mixed and then immediately filter-pressed. A clear, bright juice is thus obtained, which needs no sulphuring or bone-black filtration, but can be at once concentrated, and

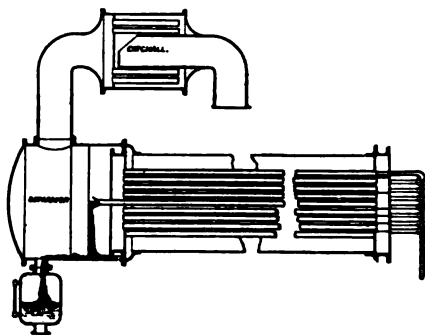
FIG. 39.

the press-cakes, after washing, make excellent fertilizer material. Lignite filtration has also been tried in the clarifying of molasses, but with little success as far as cane-sugar molasses is concerned.

The most important improvement in the preparing of a better-grade sugar, however, consists in the use of the vacuum-pan, by means of which the concentration can be effected with the least heating, and hence least discoloring of the sugar-containing juice. The vacuum-pan, invented in 1813 in England by Howard, allows of the concentration, or "boiling to grain," being effected at temperatures varying from 130° to 170° or 180° F., instead of the 240° or 250° F. reached in the open-pan. They are of varying forms, but consist essentially of a spherical, cylindrical, or dome-shaped copper or iron vessel, such as is shown in Fig. 39. The contents of this vessel are heated by the steam-coils shown in the cut, and the vacuum is maintained by the connection with an injector air-pump, as shown. The vacuum-pan is connected first with an overflow vessel, or "save-all," to

FIG. 40.

collect saccharine juice thrown over, and thence with the exhaust-pump. Through suitable openings in the side of the pan the interior can be illuminated and the operations watched; samples can be withdrawn by the aid of the "proof-stick" for examination, and fresh juice can be admitted when the grain is to be built up.

In concentrating the raw juice, considerable use is made of what are called "triple effect" vacuum-pans, a series of three connected pans, in the first of which the thin juice boils under a slightly-reduced pressure and, of course, at a slightly lower temperature than in the air; the vapor from the boiling juice here passes into the steam-drum of the second pan, and readily boils the liquor here, which, though denser, is under a greater vacuum, and similarly the vapor from this liquor boils the most concen-

trated juice in the third pan, in which, by the aid of the condensing-pump, a very perfect vacuum is maintained. Thus large quantities of juice are evaporated with great economy of fuel. "Double effects" are also used in the same way. These triple effects have been much improved in the last few years by the modifications introduced by Yaryan and Lillie, both of whom adopt the plan of sending the sugar juice to be concentrated through the series of coils while the steam circulates around these tubes. A general view of a Yaryan quadruple effect is given in Fig. 40, in which the compact arrangement of the evaporators is well shown, while the action of the Yaryan apparatus will be understood from Fig. 41, giving a simplified section through one of the pans and "catch-alls." The heating-tubes, surrounded by steam, are divided into units or sections, consisting of five tubes coupled at the ends so as to form one passage. Of such sections there may be any number. The liquor enters the first tube of the coil in a small but continuous stream, and immediately begins to boil violently. It is thus formed into a mass of foam, which contains, as it rushes along the heated tubes, a constantly-increasing portion of steam. The mixture is thus propelled forward at a high velocity, and finally escapes into an end chamber known as a "separator," which is provided with baffle-plates.

Fig. 41.

The "masse-cuite" having been brought to sufficient thickness, the whole or a part of the contents of the pan are "struck off." If half the contents of the pan are discharged and fresh syrup then admitted to be concentrated, the crystals obtained at first grow by the deposit from the new portion of syrup. This process of admitting successive portions of fresh syrup after the "grain" has once formed is used in the development of large crystals. It must be used with judgment though, or the new syrup starts a new set of minute crystals, making what is called "false grain." The large yellow Demerara crystals are given the light yellow bloom by admitting sulphuric acid in small amount after the grain is complete and just before the "strike." It destroys the gray-green color of the raw-sugar crystals and gives instead a pale straw color.

After the "masse-cuite" has left the pan, the crystallization, except in the case of the large crystals, is completed by cooling, and the sugar must then be "cured." This is now generally effected in centrifugals or rotary perforated drums. A form in common use for sugar-work is shown in Fig. 42. Over each centrifugal is a discharge-pipe from the coolers; the brown or yellow magma is let in, the inner drum is started revolving, and the mass heaping against the perforated sides becomes rapidly lighter in color as well as more compact; the syrup flies off, and from the space between the inner and outer drums runs off below into the proper receptacle. The centrifugal is emptied through the bottom of the drums by raising the central spindle and with it the detachable plates around it, so that a circular opening is made in the middle of the apparatus.

A serious loss of sugar in the usual method of working is in the scums,

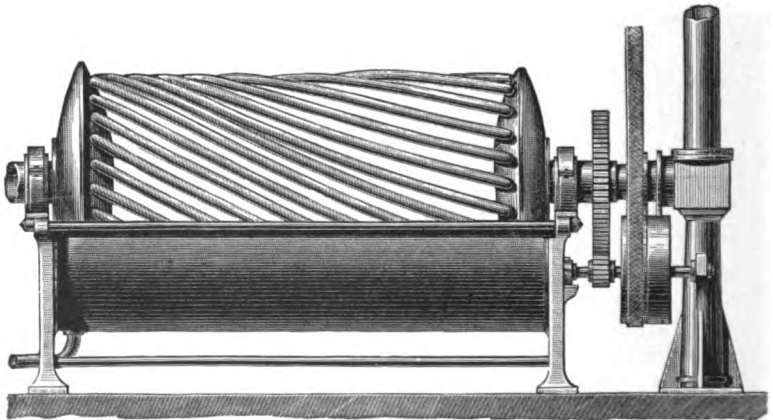
which are frequently thrown away. Professor Wiley, the chemist of the Department of Agriculture, has shown * that in working a crop of 9063 tons of cane the loss of sugar in the scums, if thrown away, would have amounted to 120,316 pounds, of which 94,545 pounds would have gone in the blanket-scums, and 25,771 pounds in the subsequent scums. To save this sugar, the scums are steamed and then pressed and washed in a filter-press (see p. 144), whereby, practically, the whole of the sugar can be recovered. The scums are generally filter-pressed now in the best Cuban and Louisiana sugar-houses, although a cruder method of pressing them in bags is used on some plantations. The application to cane juice of the method so generally followed in the case of beet-sugar of adding an excess of lime, which, after the the first boiling up, is removed by the process of carbonatation or saturating with carbonic acid gas, has generally been considered to be impossible, because, as was stated before, an excess of lime acts injuriously upon any glucose present and darkens the juice. But if the juice is from sound canes in which the glucose percentage is not large, the advantages of the carbonatation process may exceed the injurious effects. This seems to have been shown by the experiments of the Department of Agriculture at Fort Scott, Kansas, in the fall of 1886.† The yield of sugar in the experiments in which both diffusion and carbonatation were followed was, as mentioned before, larger than had ever been gotten from sugar-canes.

FIG. 42.

* Bulletin of Department of Agriculture, No. 5, p. 59. † Ibid., No. 14, pp. 52 and 53.

Professor Wiley sums up the advantages of the process as follows: "The process of carbonatation tends to increase the yield of sugar in three ways: (1) It diminishes the amount of glucose. This diminution is small when the cold carbonatation, as practised at Fort Scott, is used; yet to at least one and a half its extent it increases the yield of crystallized sugar. (2) By the careful use of the process of carbonatation there is scarcely any loss of sugar. The only place where there can be any loss at all is in the press-cakes, and when the desucration of these is properly attended to the total loss is trifling. The wasteful process of skimming is entirely abolished, and the increased yield is due to no mean extent to this truly economical proceeding. (3) In addition to the two causes of increase already noted and which are not sufficient to produce the large *rendement* obtained, must be mentioned a third, the action of the excess of lime and its precipitation by carbonic acid on the substances in the juice which are truly melassigenic. Fully half of the total increase which the experiments have demonstrated is due to this cause. It is true, the coefficient of purity of the juice does not seem to be much affected by the process, but it is evidence that the treatment to which the juice is subjected increases in a marked degree the ability of the sugar to crystallize. This fact is most abundantly illustrated by the results obtained. Not only this, but it is also evident that the proportion of first sugars to all others is largely increased by this method. This is a fact which may prove of considerable economic importance."

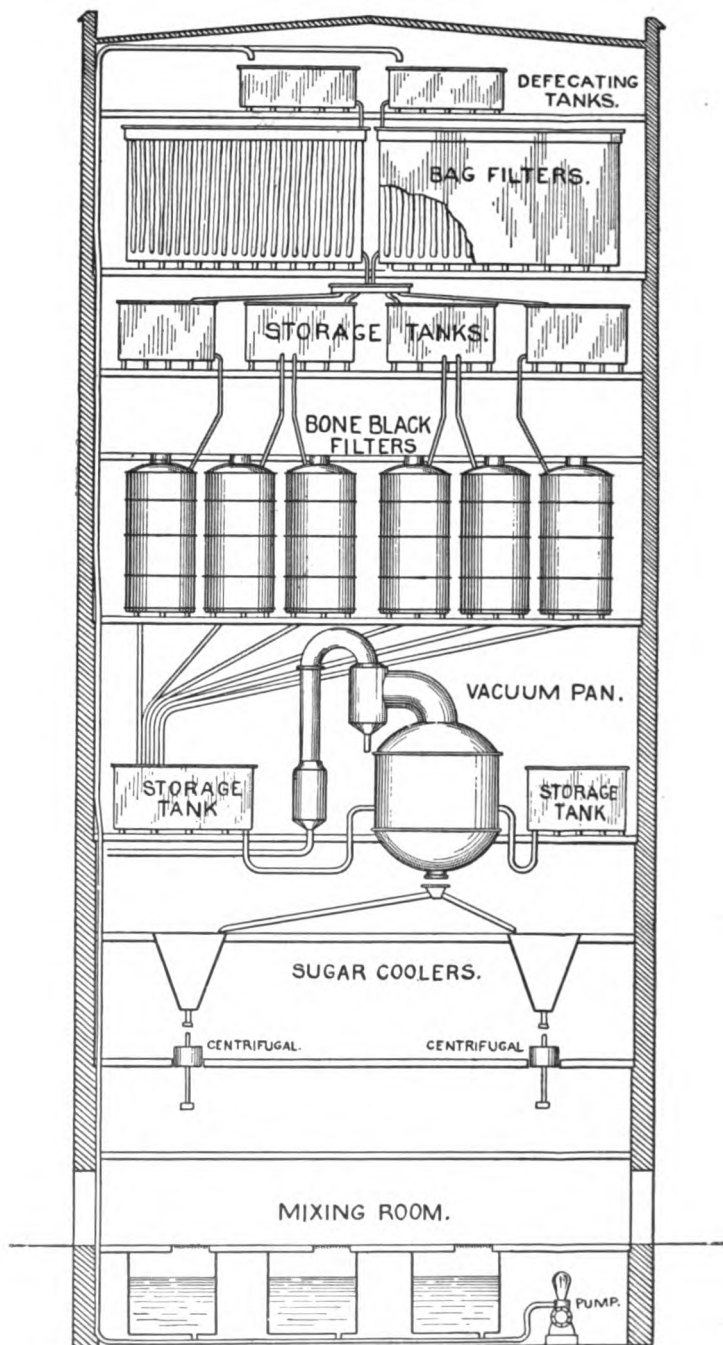
It only remains to notice in connection with raw sugars two forms of apparatus for concentrating raw-sugar juice which have had considerable use

FIG. 43.

in the tropics. The first of these is the "Wetzel pan," an apparatus shown in Fig. 43. As seen, it consists of a pan containing the liquor, in which dip pipes heated by steam passing through them; while the cylinder, formed by these pipes, is caused to revolve by power applied from the end as shown in the cut. The large heating surface enables steam at very low pressure to be used, exhaust steam from the cane-mill engine being sometimes used for the purpose. Such pans are used on some plantations, in the absence of a vacuum-pan, to finish the concentration begun in the battery or copper-wall. The liquor is brought to them at a density of 26° to 27° B. The other form of apparatus referred to is the "Fryer Concretor," in which no

attempt is made to produce a crystalline article, but only to evaporate the liquor to such a point that when cold it will assume a solid (concrete) state. The mass is removed as fast as formed, and being plastic while warm it can be cast into blocks of any convenient shape and size, hardening as it cools. In this state it can be shipped in bags or matting, suffering neither deliquescence nor drainage. The "concretor" consists of a series of shallow trays placed end to end and divided transversely by ribs running almost from side to side. At one end of these trays is a furnace, the flue of which runs beneath them, and at the other end a boiler and an air-heater, which utilize the waste heat from the flue, employing it both to generate steam and to heat air for the revolving cylinder. The clarified juice flows first upon the tray nearest the furnace, and then flows down the incline towards the air-heater, meandering from side to side. While flowing thus it is kept rapidly boiling by means of the heat from the furnace, and its density is raised from about 10° B. to 30° B. From the trays it goes into a hollow revolving cylinder full of scroll-shaped iron plates, over both sides of which the thickened syrup flows as the cylinder revolves, and thus exposes a very large surface to the action of hot air which is drawn through by a pan. In this cylinder the syrup remains for about twenty minutes and then flows from it at a temperature of about 91° to 94° C., and of such consistency that it sets quite hard on cooling.

Raw sugars are often gotten now of sufficient purity to allow of their immediate use without further treatment. Such is not the usual rule, however, but they have to undergo a purifying or refining in order to bring them to the requisite purity for consumption. The sugar-refining process is simpler in its theory than the process of preparing the raw sugars, but requires more exactitude in its execution, and more elaborate and costly machinery and equipment. The problem as stated is a much simpler one than was that of handling the raw cane juice; it is now simply a redissolving of the impure crystalline mass of raw sugar, freeing the solution from impurities, and then crystallizing afresh the pure sugar from it. The sugar refinery located in a large commercial centre is almost always a building of considerable height, so as to allow of the descent by gravity of the sugar solutions from floor to floor as the process of treatment proceeds. The general outline of the treatment will be easily followed with the aid of the diagram in Fig. 44. The raw sugars as they arrive are discharged from hogsheads or bags in the mixing room on the ground floor through wide gratings into the melting tanks, or "blow-ups," just below, where boiling water and steam rapidly dissolve all that is soluble in the sugars. These tanks hold from three thousand to four thousand five hundred gallons, and treat from nine to thirteen tons of sugar at a time. The hogsheads and bags are similarly cleaned out by live steam. The crude-sugar solution, run through a coarse wire strainer to remove mechanically-mixed impurities, is then pumped to the defecating tanks at the top of the building. The defecating is not done, as was the case with raw juice, with lime, but with some form of albumen, as bullock's blood, which, coagulating by the heat, encloses and carries with it much of the fine suspended impurities. Fine bone-black is also sometimes added along with the blood. The contents of these defecating tanks are boiled up and agitated thoroughly for from twenty minutes to half an hour, when the clear liquor is run off in the troughs leading to the bag-filters. These are of coarse, thick cotton twill, four or five feet long, and but a few inches through. These filters collect the fine suspended slime

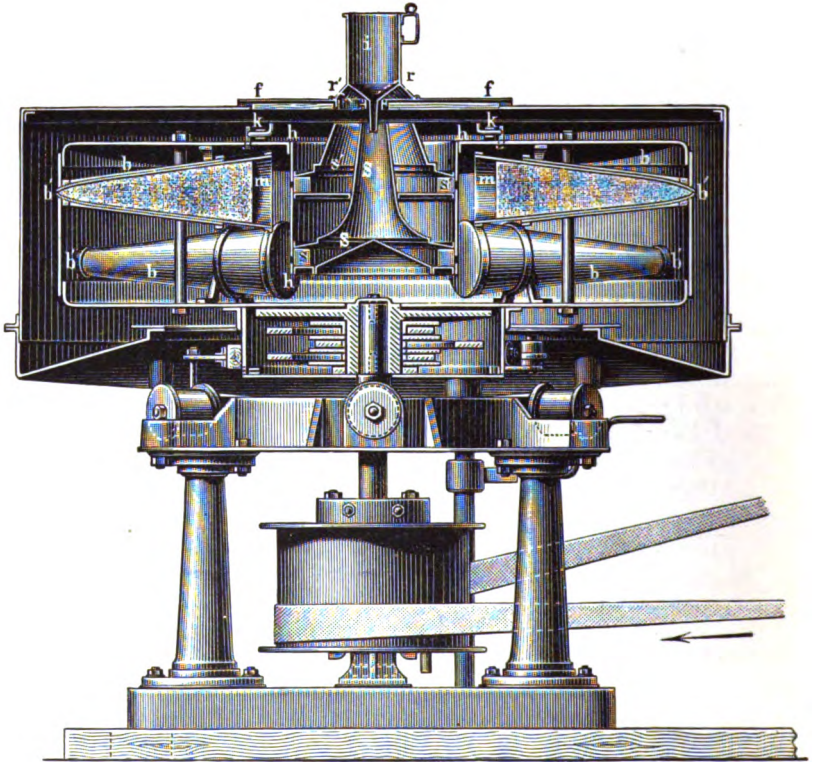
Fig. 44.

DEFECATING TANKS.
BAG FILTERS.
STORAGE TANKS.
BONE BLACK FILTERS
VACUUM PAN.
STORAGE TANK
STORAGE TANK
SUGAR COOLERS.
CENTRIFUGAL.
CENTRIFUGAL
MIXING ROOM.
PUMP.

which would not settle in the defecating tanks. It has been found impossible to replace them by filter-presses in the working of the raw cane sugars at present in the market, on account of the slimy character of the separated matter. The liquor, now containing soluble impurities only, has a brown color. It goes from the storage-tanks below the bag-filters to the bone-black-filters. These filters, immense iron tanks, twenty feet high and eight feet in diameter, open through man-holes at the top to the filter-room floor. They have false bottoms, perforated, over which a blanket is fitted to prevent the bone-black from flowing through with the liquid. The largest filters hold thirty to forty tons of the bone-black. When they are filled with bone-black the man-hole is closed, and the syrup from the cisterns below the bag-filters is turned on. It percolates slowly down, is allowed some time to settle, and after about seven hours the drawing off begins through a narrow discharge-pipe. The filtered syrup is caught in different tanks as it becomes deeper in color, and the colorless syrup first obtained used for the finest sugars, and so on. When the charge has run out, the sugar remaining in the charcoal is washed out by running through fresh or "sweet" water, and the bone-black must be reburned before it can again be used. From three-quarters to one and a quarter tons of black are needed per ton of sugar decolorized, according to the quality of the raw sugars. The liquor is now ready to be concentrated in the vacuum-pan and brought to the crystallizing point. This vacuum-pan boiling has already been described under raw sugars. The processes of boiling are somewhat different for "mould" and for "soft" sugars. The best grades of syrup boiled to an even, good-sized grain are used for the former, whether loaf, cut, crushed, or pulverized. As the "masse-cuite" cools it is run into conical moulds with a small aperture at the bottom, or smaller end, through which the uncrystallized liquid may drain off. After this has been allowed to drain, water or white syrup is poured in at the top, which washes the crystals as it slowly filters through. After a sufficient time allowed for drainage, the moulds are turned over, so that the small quantity of syrup in the point of the cone shall distribute itself through the mass. The result is the hard white "sugar-loaf," or conical form of sugar. The process of draining in moulds is, however, very generally replaced by the use of large centrifugals, in which several cones can be dried at a time in a few minutes, saving enormously in time and in the room previously occupied by the large number of moulds needed for several days' working. Such a hydro-extractor for cones is shown in Fig. 45. The "soft" sugars, the crystallization of which is completed in the cooler after the "masse-cuite" leaves the vacuum-pan, are cured mostly by centrifugals, and are ready for barrelling on leaving them.

2. Production of Sugar from the Sugar-beet.—In considering the question of the production of sugar from the sugar-beet, two things must be noticed: first, the soft, pulpy character of the beet, which allows of much more complete extraction of the juice, and, second, the more complex composition of the juice, which necessitates more elaborate methods of purification of the juice.

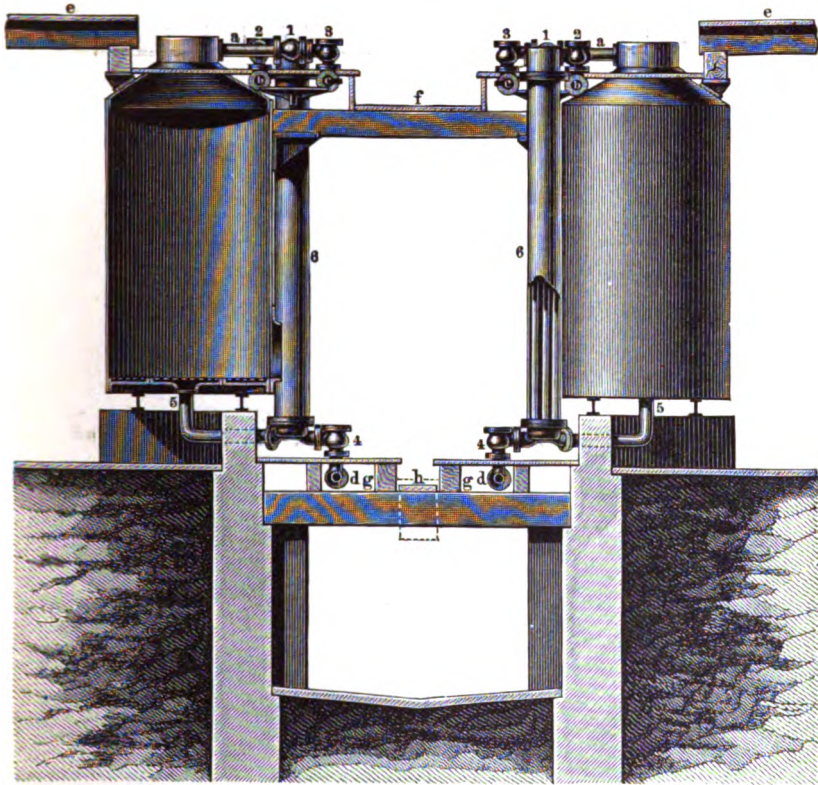
The cultivation and working of the sugar-beet has been developed to so much greater an extent in Germany than any other country that we shall, in describing the extraction of sugar from the beet, notice German methods chiefly. The beets are first washed, brushed and deprived of the tops, and then made to yield their juice by one of four methods: (1) by pulping them and pressing the pulp either in hydraulic presses or between rolls; (2) by

centrifugating the pulp; (3) by the maceration process, in which the pulp is exhausted with either warm or cold water, and the residue pressed; and (4) by the diffusion process, in which the beets are not pulped at all, but are cut into thin transverse sections, known in Germany as "schnitzel," in France as "cosettes," and in English as "chips." These are then put into a series of vessels, in which a current of warm water is made to displace the sugar juice by the principle of "osmosis," or diffusion, as it is more generally called. The first three processes are now almost entirely displaced in Germany by the diffusion process. It is obvious that in this latter the juice will be freer from the fine mechanically suspended impurities and

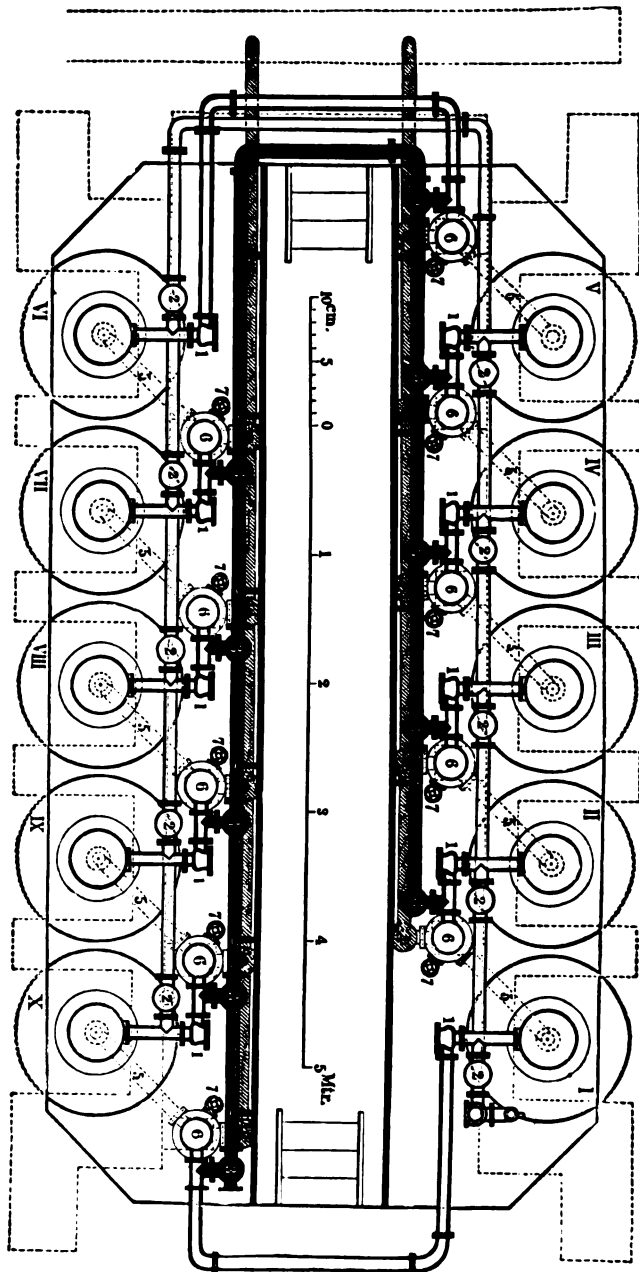
Fig. 45.

solid particles than in the processes that rupture the cell-walls. In this country the beet-sugar factories have all been equipped with diffusion batteries of approved construction, and that method has been the one exclusively employed. In France the diffusion method has not become so generally popular. As, however, it yields a purer juice and a higher percentage of the same than the older methods, and is, as just stated, the one that is displacing the others, we shall confine ourselves to it.

In the diffusion method of Robert, the fresh beets are cut into slices or "chips" of about one millimetre thickness, which are digested with pure water at from 50° C. to 60° C. This allows the saccharine beet juice to pass through the cell-walls and mix with the water and the water to replace it

in the cells, while the colloid non-sugar remains behind. The vessels used for this diffusion are mostly upright iron cylinders, as shown in Fig. 46, which are provided with a man-hole above for charging them with the chips. A series of these diffusors connected together is known as a battery. They are brought to the proper temperature either by a small steam-coil on the bottom of the vessel or by so-called "calorisators," or juice-warmers, detached upright heating vessels inserted between every two diffusors. A

Fig. 46.

diffusion-battery of ten cells, with juice-warmers, is shown in plan in Fig. 47. From the bottom of each cell, *I* to *X*, goes a delivery-tube, 5, to the bottom of the juice-warmer, where it divides into seven tubes. From the top of each juice-warmer a tube, *a*, bent at right angles, connects with the next cell. The connection of the opposite cells, *V* and *VI*, as well as the cells *X* and *I* at the other end, is effected, as shown in the ground-plan, by longer tubes making these bends at right angles. By suitable valves in the supply- and delivery-tubes each cell can be shut off from the others. The upper man-holes of the cells are all reached from the platform *e*, which runs along just above them; the valves 1, 2, 3 are reached from the platform *f*, which runs along lower down, supported on cross-pieces, as shown in Fig. 48; and the third platform, *g*, gives access to the lower valves. A sunken canal, *h*, in this lowest platform allows of the exhausted chips being discharged from the lower man-holes on to an endless band, which passes

around two wheels and delivers them into ascending buckets, whence they go to the chip-press, which dries them. The filling of the cells is effected

FIG. 47.

by means of a swinging trough, not shown in the cut, connecting with a chip-cutter placed on a higher level.

In operating the battery, water at 66° C. is run into the first cell, which has been previously filled with fresh chips. For every cubic metre of space four hundred and fifty kilos. of chips and five hundred kilos. of water are to be reckoned. The cell remains quiet for twenty minutes, during which time the temperature falls to 45° C. The connection with the neighboring juice-warmer is now opened, and the thin juice made to pass into this by forcing fresh cold water into the first diffusion-cell. The juice, brought in the warmer to 66° C., is then passed into the second cell, which has been filled with chips. After twenty minutes the juice in No. 2 is passed into the adjoining juice-warmer, while the cell fills up with the juice from No. 1, and this in turn with fresh water. No. 3, which had been filled meantime with chips, is now brought into the connection. After the juice has been kept in contact, at 66° C., with the contents of each of the three cells in turn for twenty minutes, it is sufficiently concentrated to go to the defecating pan. This juice is therefore sent to be purified, while No. 3 fills up with the thin juice from No. 2. In twenty minutes this is displaced, and, after being warmed to 66° C., goes to No. 4, a freshly-filled cell. After suitable action here it goes direct to the defecating pan, as it is the second diffusate of three cells and the first of a fourth. From this time on, as a new cell comes into operation the juice from one cell goes to the defecating pan until the ninth is in connection, when the first cell is disconnected and emptied of the exhausted chips and then filled with fresh. While this is going on the tenth cell has been connected; and then the second is to be emptied, while the first cell is brought into connection with the tenth. Thus nine cells are always working together in the battery, while the tenth is disconnected for emptying and filling.

The diffusion-cells are sometimes arranged in a semicircle or a circle instead of a straight line, as this arrangement is thought to be more convenient when the cells are to be filled and emptied. Such a circular diffusion-battery is shown in Fig. 48, and the method of filling the cells with the chips or slices is shown, as well as the endless belt carrying up the buckets of exhausted chips to be emptied. A continuous diffusor, consisting of one long cell, in which the chips and water move in opposite directions, so that as the juice becomes more concentrated it shall meet chips richer and richer in sugar, has also been devised.

As stated, the percentage of extraction by these methods is higher and the juice is purer than by any other method, while the dried chips also serve as most valuable fertilizer material or for cattle food. Their average composition is: ash, 5.67; fat, .49; crude fibre, 23.36; crude protein, 8.70; and non-nitrogenous extractives, 61.78. A modification of this diffusion process by Bergreen, already found advantageous in practice, is to exhaust the cells of air after filling them with fresh beet-chips, and then to allow expanded steam to enter, so as to coagulate the albuminoids. The usual procedure then follows. The exhausted chips gotten this way make a good cattle food, as they are richer in nitrogenous matter. The beet juice, by whichever of the four methods before mentioned it may be gotten, is now to be purified. The general outlines of the method of working up the juice is shown on the accompanying diagram, based on that of Post,* but modified to accord with recent improvements. Except in the case of the diffusion juice of Bergreen's process mentioned above, the crude juice is heated by

* Post, Chemische Technologie, ii. p. 274.

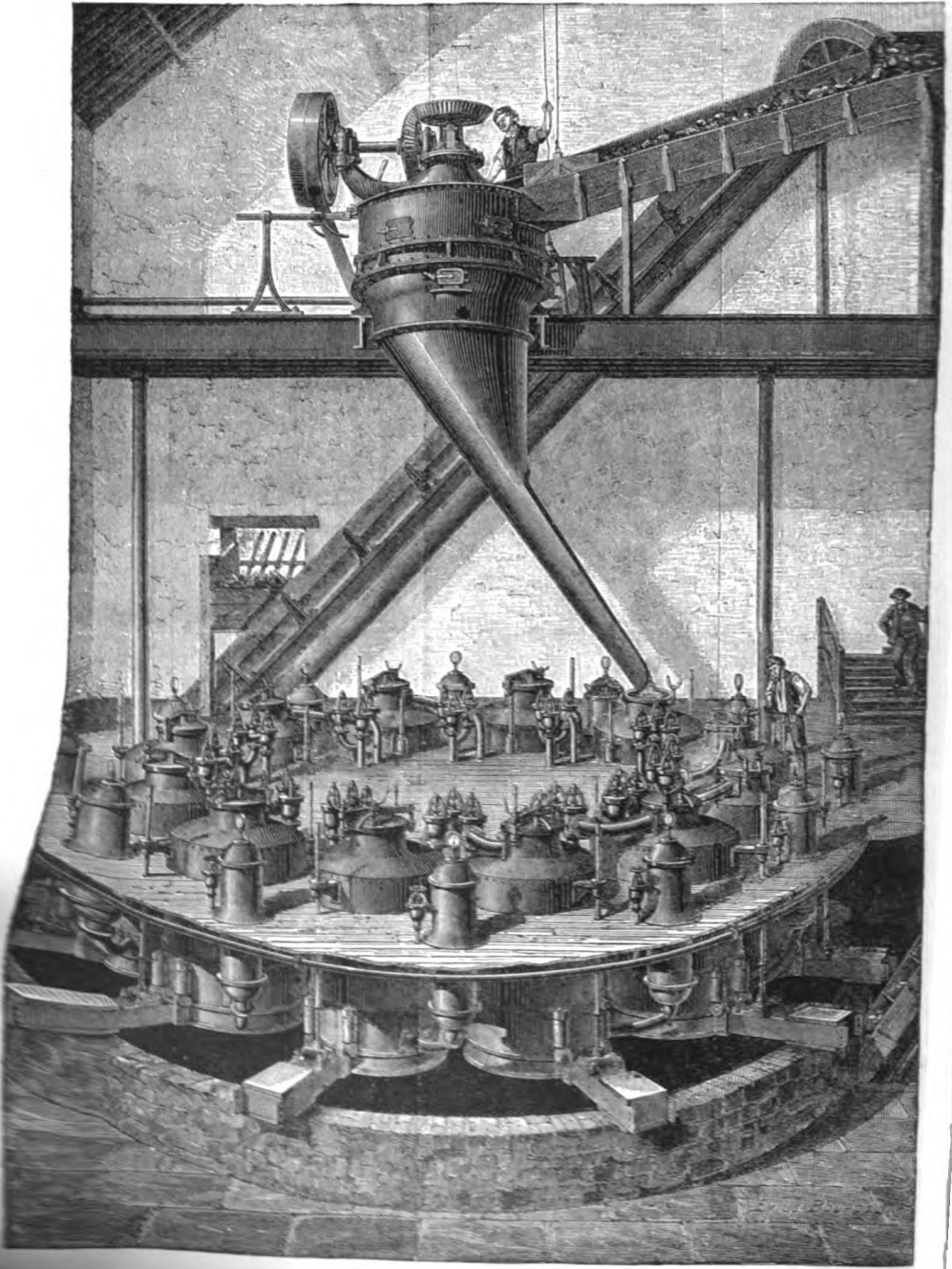
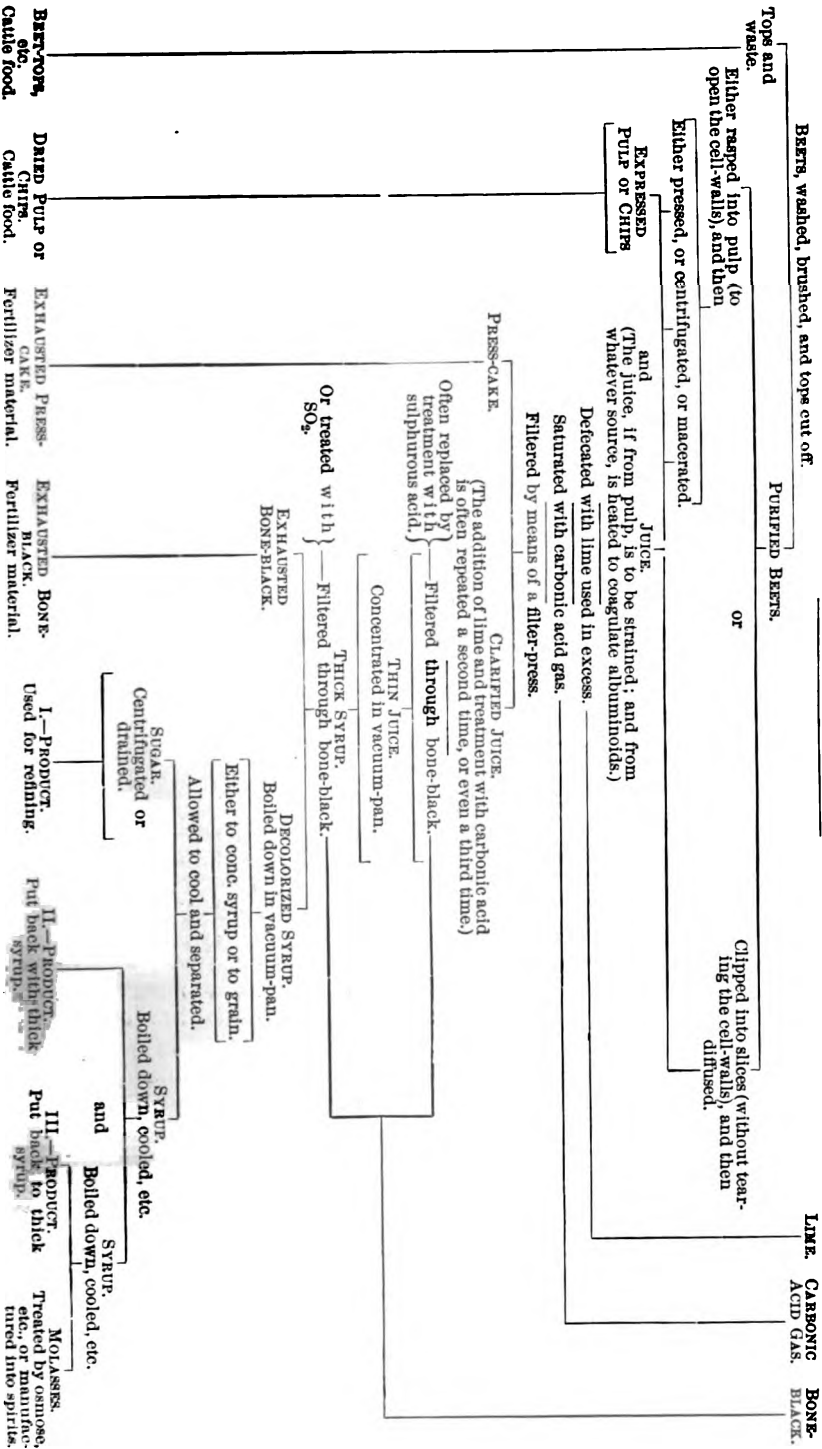
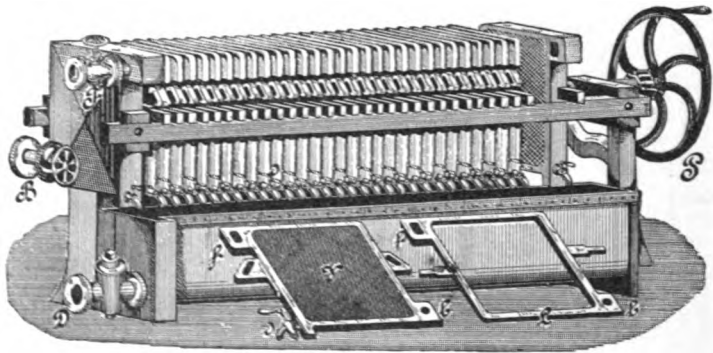
FIG. 48.

# TABULAR VIEW OF THE WORKING OF BEET-SUGAR.

indirect steam to 80° C. to coagulate the albuminoids, and then two to three or even four per cent. of caustic lime, in the form of milk of lime, is added. This lime saturates the free acids and throws out nitrogenous compounds as in the case of cane juice, and, because of its excess, forms soluble calcium saccharates with some of the sugar. Carbonic acid gas is then added until the precipitated carbonate of lime becomes granular and settles readily. At this time there still remains a slight excess of free lime,—about .1 to .2 per cent. The contents of the saturation-pan are now pumped into the filter-presses and the press-cakes washed free from sugar by steam. A filter-press, such as is adapted for sugar-scums and carbonatation press-cakes, is shown in Fig. 49. This treatment is called the first carbonatation. The juice may be filtered now at once through bone-black, which will withdraw the remaining lime as well as decolorize it, but in most German sugar-houses it is subjected, boiling hot, to a second treatment with one-half per cent. of lime, and then completely neutralized with carbonic acid. This is called the second carbonatation, or the *saturation*. After again going through the filter-press the juice goes to the bone-black-filters. In many of the newer German sugar-houses the filtration of the thin juice through bone-black is no longer

FIG. 49.

practised, as repeated saturations with lime and carbonic acid or treatment with sulphurous acid and sulphites have so clarified it as to make bone-black unnecessary. It is stated that at Watsonville, California, in the beet-sugar factory of Spreckels, bone-black filtration is thus dispensed with. The thin filtered juice is concentrated in double or triple effect vacuum-pans to 24° or 25° B., and then filtered again as thick juice through bone-black. This second filtration takes the last traces of nitrogenous materials out, and the remnant of lime which remained in solution. It is then concentrated in the vacuum-pan to crystallization.

In the preparation of raw sugar, the "masse-cuite" is dropped from the vacuum-pan into small coolers of about two hundred kilos. capacity, in which it becomes cold and crystallization is completed. The contents of these coolers are then mixed and broken up and rubbed to a paste with the aid of some syrup, and the whole centrifugated. The sugar so obtained is the raw beet-sugar of commerce. The syrup obtained is concentrated in a vacuum-pan, and the sugar from this forms the second product, which sometimes goes into commerce and sometimes is returned to the thick juice to be worked up with it.

As was stated before, raw cane-sugar can be obtained by care and with the best vacuum-pan practice so nearly pure as to be directly available for use without any special refining. In the case of raw beet-sugar this is much more difficult. The raw beet-sugar, though it may be well crystallized, usually contains substances of decidedly unpleasant odor and taste, chiefly decomposition products of the betäine of the juice (see composition of the beet, p. 123), which are in the syrup adhering to the crystals. The production of a well-crystallized sugar for consumption direct from the beet juice requires, therefore, a thorough cleansing of the crystals in the centrifugating process. This is accomplished by the purging of the crystals with a clear white syrup, which displaces the impurer syrup adhering, or very generally by the use of steam of low tension either admitted into the inner drum of the centrifugal or to the space between the revolving drum and the mantel. In this last case the steam does not so much cleanse the crystals as it warms the mass and liquefies thoroughly the syrup in the spaces between the crystals. The production for direct consumption of a commoner sugar, known in Germany as "melis," or lump-sugar, is an important branch of the raw sugar-working. In this case the contents of the vacuum-pan brought to grain, but without the special building of crystals, are discharged into shallow vessels with false bottoms, which may be called "warmers," in which the "masse-cuite" is heated up from 60° to 90° C., which has the effect of redissolving most of the small crystals. The warmed syrup is now filled into the moulds, in which it crystallizes uniformly to a compact whole. This grade of sugar would have as so produced a light yellow color, which is usually corrected by the addition of ultra-marine blue.

Of course, raw beet-sugar can be most advantageously purified by a complete refining process, analogous to that described under cane-sugar, in which they are redissolved, clarified, decolorized, and again crystallized. The procedure is so similar to that described under the refining of cane-sugar that it need not be specially noticed here.

3. THE WORKING UP OF THE MOLASSES.—It is stated in the tabular view of the working of cane-sugar on p. 127, that the molasses is used for syrup or worked over into molasses sugars. We should distinguish, however, between the several grades of molasses. In working up the raw sugar reference was made to first, second, and third sugars. Corresponding to each of these three grades, of course, is a different molasses, sometimes known as first, second, and third molasses, and sometimes as second, third, and fourth molasses. The average percentage of sucrose and of reducing sugars in these is shown from the analyses of the United States Department of Agriculture * made at Magnolia, Louisiana, in 1884.

| | | |
|---|---|---|
| First molasses . . | Sucrose, 37.97 per cent. | Reducing sugar, 8.13 per cent. |
| Second molasses . | Sucrose, 41.23 per cent. | Reducing sugar, 18.82 per cent. |
| Third molasses . . | Sucrose, 21.87 per cent. | Reducing sugar, 21.06 per cent. |

The percentage of solid non-sugar in the first and second of these molasses will nearly, if not quite, equal that of the sucrose, while in the third it considerably exceeds it.

The "first molasses" is sufficiently pure to be mixed with syrup sugar in the pan for the production of a second product sugar; the "second

* Bulletin No. 5, p. 52.



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molasses" can be refined as such for brown or grocery sugars, and the "third molasses" is so sticky and impure that it can only be sent to the rum-distillery, where it is fermented for rum. (See p. 219.)

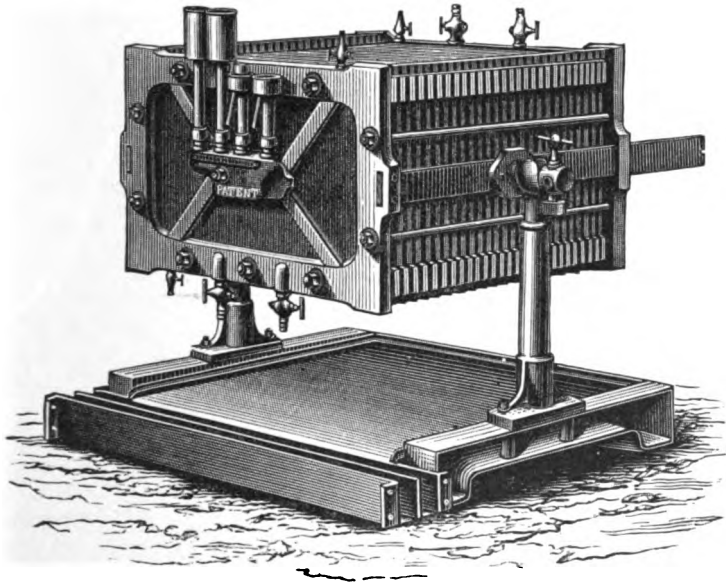
With respect to beet-root molasses the case is different. It is very impure from mineral salts and nitrogenous materials, but is nearly pure from the invert or reducing sugar so abundant in cane-sugar molasses, and in recent years it has been found possible to work it specifically for the extraction of the sucrose, of which over ninety per cent. is now extracted, thus reducing the loss of sugar to a minimum. The average composition of beet-sugar molasses is given at fifty per cent. of sucrose, thirty per cent. of non-sugar, and twenty per cent. of water. Of these thirty non-sugar, ten are made up of inorganic salts, chiefly potash compounds, and twenty of organic non-sugar (see composition of the sugar-beet, p. 123). As the amount of beet-sugar molasses produced in Continental Europe annually is estimated at 250,000 tons, the fifty per cent. of sucrose represents 125,000 tons of sugar which it was certainly desirable to extract if possible. The processes for accomplishing this depend upon either one or the other of two principles: either to withdraw from the molasses the potash and other mineral salts which prevent the crystallization of the sucrose, or to precipitate out the sucrose in combination with calcium or strontium as an insoluble sucrate, which is then mixed with water and decomposed by carbon dioxide or used in the defecation of beet juice instead of lime.

The elimination of the potash salts may be effected, according to Newland's proposal, by the addition of aluminum sulphate so as to form potash alum, which is crystallized out, or by the "osmose" process, in which the principle of diffusion already referred to (see p. 138) is again made use of. In this case advantage is taken of the fact that the potash salts are the most crystalline constituents of the molasses, and hence will pass through a sheet of vegetable parchment more rapidly than the other constituents. So if the molasses warmed to 80° or 90° C. be made to pass in a stream on the one side of such a membrane while pure water passes on the other, the potash salts diffuse through, and are to that degree eliminated from the molasses. However, the difference in the rapidity of diffusion of the salts and the sucrose is not sufficiently great to allow of a very perfect separation, so that to avoid loss of sugar the operation must be stopped before the elimination of salts is complete. A little more than half of the sugar can be recovered from the molasses in this way. The apparatus in which this treatment of the molasses is carried out is known as an osmogene, and is illustrated in Fig. 50. It consists of a number of very narrow but high and deep cells adjoining each other, the sides of which are of parchment paper. Through alternate cells in this system goes the heated molasses, and through the intervening cells the water at the same temperature, each connecting with lateral canals for the supply and withdrawal of the respective liquids. The ordinary osmose apparatus of the German sugar-houses is capable of working 1000 kilos. or upwards of molasses per day, and at a cost of 1.60 marks (38.4 cents) per 100 kilos. of molasses. The osmose sugar is somewhat darker in color than ordinary second or third sugar, but is of pleasanter and sweeter taste. The yield of the osmose process varies with the grade of the molasses taken; a molasses with a purity coefficient of fifty-eight to sixty will yield ten to twelve per cent. of the molasses taken, and one of a coefficient of sixty to sixty-five will yield seventeen, or sometimes as high as twenty, per cent. By repeating the

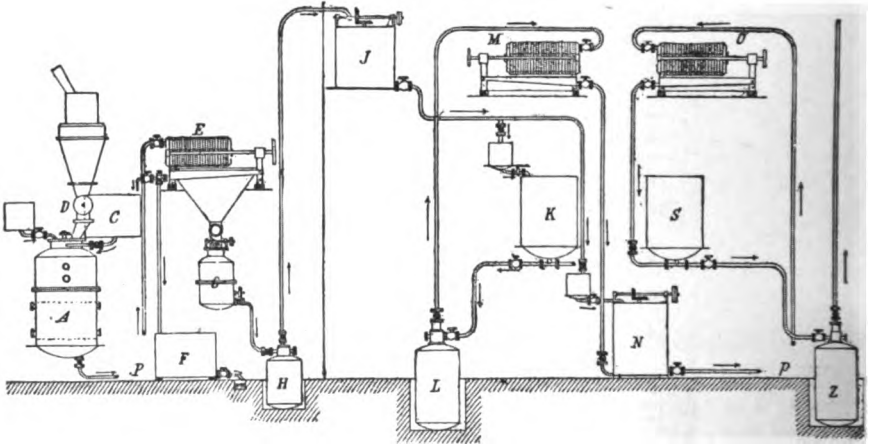
osmose process thrice the yield can be raised to thirty per cent. out of the possible fifty per cent. of sucrose contained in the molasses.

Of the methods depending upon the formation of a lime or strontia sucrate, the most important are the Scheibler-Seyferth elution process, the Steffen substitution and separation processes, and the strontium processes.

In the first of these processes, finely powdered quicklime is added to the molasses, which has been previously concentrated in vacuo to 84° or 85° Brix, in the proportion of about twenty-five parts of the former to

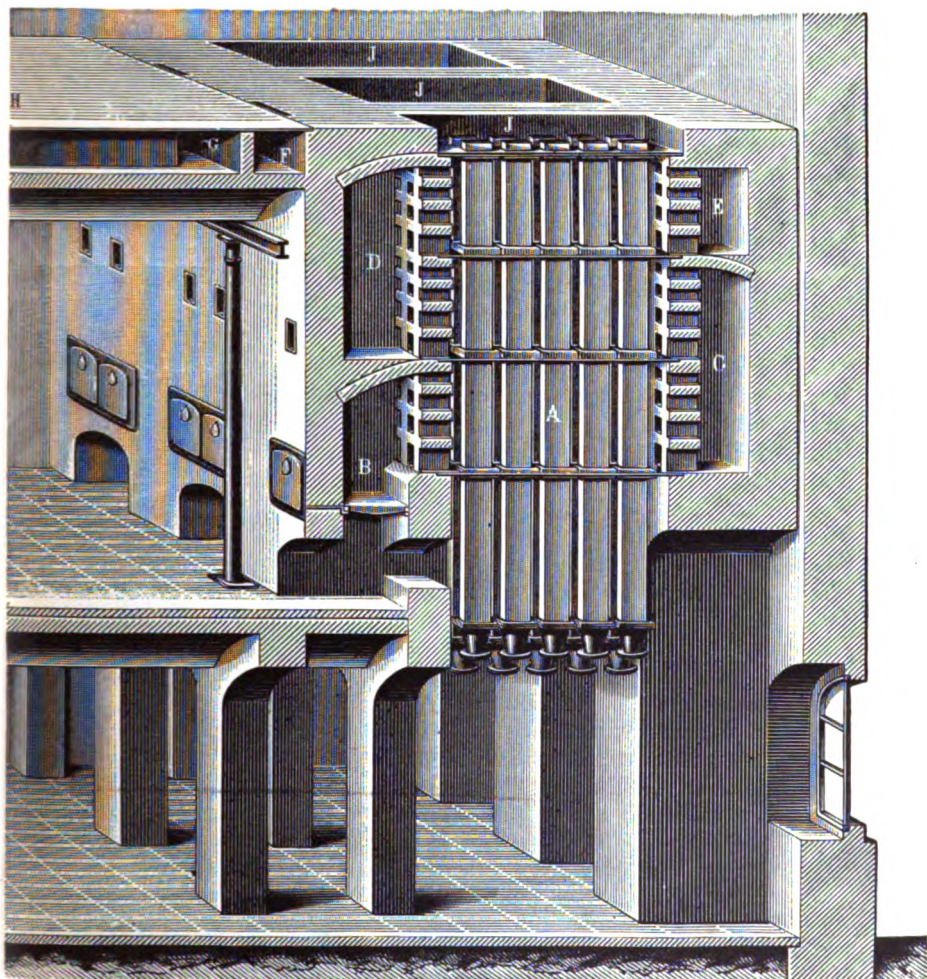
FIG. 50.

one hundred parts of the latter. The lime slakes at the expense of the water of the molasses, and leaves the tribasic calcium sucrate in the form of a dry porous mass. This is then broken up and put into the "elutors," vessels which are somewhat similar in design to the cells of a diffusion-battery. The impure sucrate is here systematically washed with thirty-five per cent. alcohol, which dissolves away from it most of the adhering impurities. The washed sucrate is then brought to the condition of a fine paste with water, and either decomposed with carbon dioxide or used instead of lime in treating fresh beet juice. This process takes out eighty-five to ninety per cent. of the sugar contained in the molasses, but the cost is somewhat greater than in the case of the osmose process. The alcohol is recovered from the washings by distillation. Steffen's substitution process depends upon the difference in solubility of the tricalcium sucrate at high and low temperatures. The molasses is first diluted so that it shall contain about eight per cent. of sugar, and then caustic lime added until some two to three per cent. has been used. The whole mass is then heated to 115° C., when the tricalcium sucrate is precipitated and separated by the use of a filter-press. The sucrate is ground up, again filter-pressed, and then can be used in defecating sugar juice. The washings from the filter-press are used to dilute a fresh quantity of molasses to the degree mentioned before,

which, treated with lime in the proper proportion and heated up, separates the sucrate, which is treated as before. After about the twentieth operation, the cooled mother-liquors and wash-waters are treated with lime alone, and the residual liquors after this treatment are then rejected. In the Steffen separation process, on the other hand, the molasses solution is kept cold, the temperature not being allowed to rise over 30° C. (86° F.). The molasses is diluted until the density shows 12° Brix, the percentage of sugar being then from seven to eight. This solution is cooled down to 15° C. (59° F.), and finely-powdered quicklime is added in small portions at intervals of about a minute, the temperature rising a little each time and being again cooled down. The mixing of the molasses and the lime, in the proportion of fifty to one hundred of powdered lime, according to quality, to one hundred of dry sugar, in the solution takes place in a closed mixing-vessel of iron provided with tubes through which cold water is kept circulating, and with a mechanical agitator to mix the contents uniformly. The insoluble sucrate separates out rapidly in the cold, and the contents of the mixer *A* (see Fig. 51) are pumped to the filter-press *E*, where the sucrate

Fig. 51.

is washed, the mother-liquor, containing all the impurities of the molasses, being put aside for fertilizing purposes, the wash-water, however, being collected in *F* for use in diluting new quantities of molasses. The washed sucrate drops from the filter-press into the sucrate-mill *G*, where it is mixed to a thin paste with water, and then pumped, by means of the monte-jus *H*, to the receptacle *J*. From here it can be sent into the first saturation-vessel *K*, and to the filter-press *M*, and to the second saturation-vessel *S*, and the filter-press *O*.

The process which at the present time is attracting very favorable attention and seems to give considerable promise is the strontium process. In this the sugar is precipitated either as monostrontium sucrate, which is quite difficultly soluble in the cold, or as bistrontium sucrate separating from hot solution. According to Scheibler's monosucrate procedure, the molasses is well mixed with hot saturated strontium hydrate solution, and the mixture passed over cooling apparatus into crystallizing tanks, where a few crystals of the monosucrate are added to start the crystallization. After

some hours the whole mass is changed into a crystalline magma, which is broken up and put through a filter-press. The white cakes of strontium sucrate go, as in the case of calcium sucrate, to the treatment of crude beet juice, while the mother-liquor is treated with more caustic strontia and boiled, when bistrontium sucrate is precipitated. This is dense enough to be washed by decantation, and then can be used instead of strontia solution

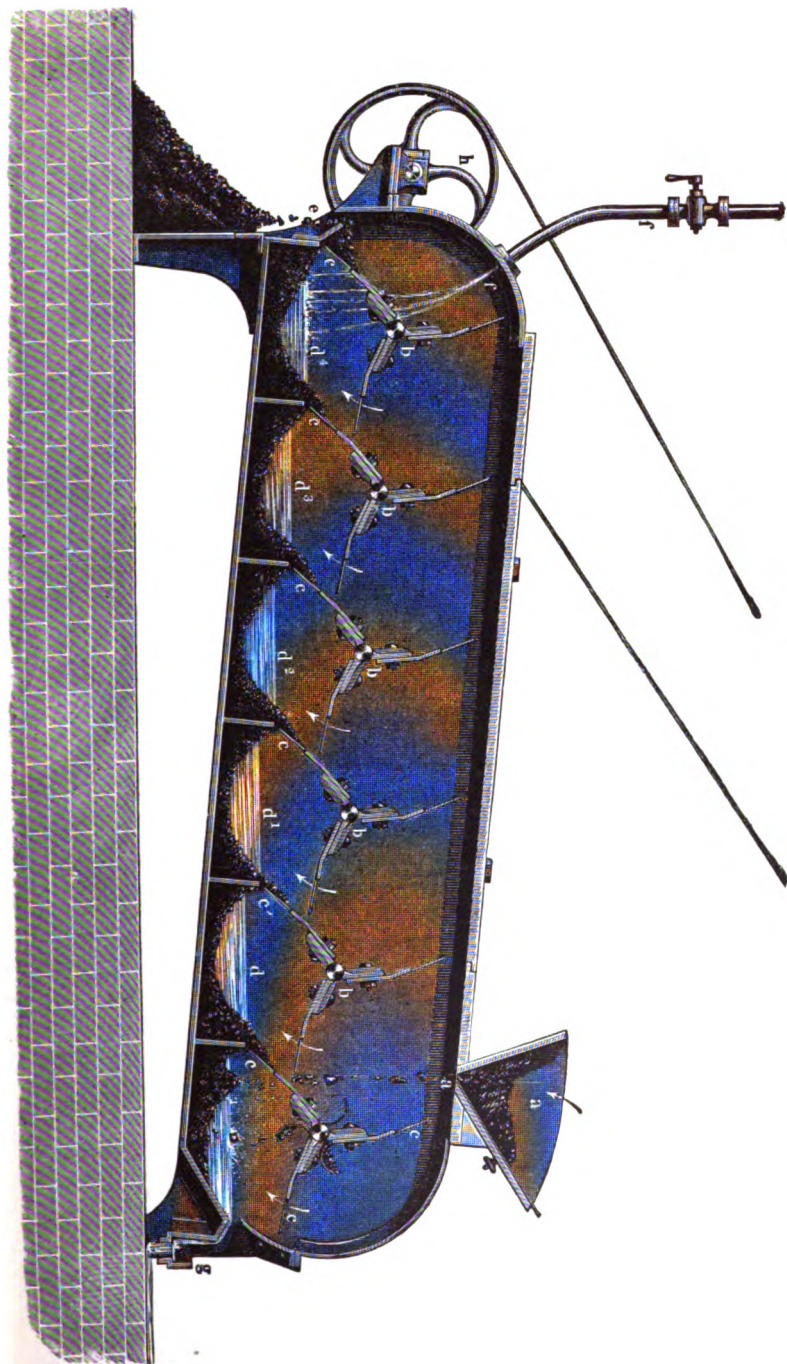
Fig. 52.

with fresh molasses for the formation of monostrontium sucrate. The excess of strontia is recovered from all the mother-liquors and worked over into caustic strontia. By the other strontium process the molasses is added to a twenty to twenty-five per cent. strontium hydrate solution, both taken hot, in such amount that for one part of sugar about two and one-half parts of strontium hydrate are present. The precipitated bistrontium sucrate separates rapidly, and the mother-liquor can be decanted from it. The

sucrate is washed with hot water or with a ten per cent. hot strontium solution. In order to decompose the sucrate, it is brought in a refrigerating chamber and cooled to 10° to 12° C., when, after twenty-four to seventy-two hours' standing, according to temperature, etc., it decomposes into crystallized strontium hydrate and sugar solution, containing something less than half of the strontia. After filtering off the crystallized strontium hydrate, the sugar-liquor is decomposed with carbon dioxide in the usual way.

In Germany in 1891–92, 48 sugar-houses extracted by the osmose process, 28 by the elution and precipitation process, 3 substitution, 20 separation, and 1 strontian process. Osmose produced 509,595 metric centners, elution 548,476 metric centners, substitution 22,015 metric centners, separation 361,149 metric centners, and the strontian process 14,765 metric centners of sugar.

4. Revivifying of the Bone-black.—The bone-black, or "char," after use in the filters, becomes charged with impurities and loses for the time its decolorizing power. It can, however, be restored to activity, or "revivified," by suitable treatment so as to be used again for filtration, and this process can be repeated many times before, by the gradual loss of its porous character and change of composition, it becomes unfit for use. In working sugars from the cane this revivification is a much simpler process than in the case of beet-sugars. In the former case, water as hot as possible is run in at the top of the filter, which displaces the sugar solution remaining in the pores of the char and forms a dilute solution of sugar and the soluble impurities taken up from the liquor. This dilute solution is known as "sweet-water," and is usually boiled down in triple effects and run in with the lower-grade products. After running additional hot water through, the filters are drained, and the moist char, after a partial drying, is put into the top of the vertical retorts, in which it is to be heated out of access of air for the decomposition of the organic matter still remaining in the pores and the restoration of its absorbent power. Various forms of char-kilns are in use in different refineries. That shown in Fig. 52 represents one of the simpler forms of char-kilns. The moist spent black from the filters in which it was washed goes on to the floor *H*, where it is dried by the waste heat passing through *G* and *F*, and then goes into the openings at *J*, which are kept always heaped up. The black descends in the retort-pipes *A* from the upper cooler portions into the middle hottest part, and then, as portions are withdrawn below, into a cooler section again. The black drawn off below is protected from the air by being received into closed receptacles or at once filled into the bone-black-filters. In other forms of kilns, the retorts are rotated slowly by mechanism so as to heat all parts equally.

In beet-sugar refineries the revivifying of the char, as before stated, is a more tedious process. This is in part because the juices and syrups have been limed in such excess in the preliminary stages of treatment, and in part because the beet juice contains much more albuminoid and organic non-sugar, which is absorbed in the pores of the char and cannot be gotten rid of by simple washing. The first step in the revivifying, then, in this case, is a treatment with a calculated amount of hydrochloric acid to remove the excess of carbonate of lime; after this a thorough washing of the black in special washing-machines, such as the Klusemann washer, shown in Fig. 53; then a fermentation to decompose into simpler and soluble constituents the absorbed albuminoids and other organic matter. The fermentation may be either what is termed the dry fermentation, in the presence of a very

Fig. 53.

small quantity of water, or the moist fermentation in the presence of a larger amount. The first takes from twelve to twenty hours, while the latter requires from six to seven hours only. The black, after the fermentation, is treated with boiling alkaline solutions, washed, and then burned in char-kilns as already described. The char seems to improve in filtering power at first, as a consequence of revivifying, but soon loses again and runs down steadily in value. This is in large part due to the separation out in the pores of carbonized residue from the burning. This carbon has no decolorizing power like the nitrogenized carbon of the original bone-black, but simply clogs the pores of the char and mechanically obstructs its action.

## III. Products of Manufacture.

1. Raw Sugars.—The composition of the juice from both the sugar-cane and the sugar-beet has been stated, and the processes for preparing the raw sugar from each of these sources. We may now examine more closely the character of the products obtained. The raw cane-sugar, made as it is chiefly in the tropics under a variety of conditions of working, from the most primitive to the most highly improved, has come into commerce under a great variety of names as well as of varying grades of purity. The raw beet-sugar is usually known as first, second, or third product sugar. (See p. 143.)

*Muscovado* is a brown sugar produced in the West Indies, generally by open-pan boiling, which has been drained in hogsheads or perforated casks, and so freed in large part from the accompanying molasses.

*Cassonade* is a name formerly applied in the French colonies to muscovado sugars.

*Melada* is a moister brown sugar, produced like the muscovado, but not drained free from molasses.

*Concrete*, or concreted sugar, is the product of the Fryer concretor (see p. 135) or similar form of apparatus, and is a compact, boiled-down mass, containing both the crystallizable sugar and impurities which ordinarily go into the molasses. It shows little or no distinct grain.

*Clayed sugars* have been freed from the dark molasses by covering them in moulds by moist clay, which allows of a gradual washing and displacement of the adhering syrup.

*Bastards* is the name given to an impure sugar gotten by concentrating molasses and allowing to crystallize slowly in moulds.

*Jaggery* is the name given to a very impure East Indian palm-sugar, sometimes refined in England, but chiefly consumed in the country of its production.

*Demerara crystals* are the product of the best vacuum-pan boiling and have been well purged in the centrifugals. They have the light yellow bloom due to treatment with sulphuric acid. (See p. 132.)

These Demerara crystals have also been brought to the United States with very dark brown color. This, however, was only superficial, and was capable of removal by centrifugating with a lighter-colored syrup. The dark color was imparted like the yellow bloom by the action of sulphuric acid added in the vacuum-pan before discharging the contents of the same.

The composition of a variety of raw cane- and beet-sugars is given in the accompanying table:

| DESCRIPTION OF SUGAR. | Sucrose. | Glucose. | Organic non-sugar. | Ash. | Water. | Authority. |
|---|---|---|---|---|---|---|
| Cane, Cuba (centrif.) . . . | 91.90 | 2.98 | 2.70 | 0.72 | 1.70 | Wigner and Harland. |
| " Cuba (muscovado) . | 92.35 | 3.38 | 0.66 | 0.77 | 2.84 | Wallace. |
| " Jamaica . . . . . . | 90.40 | 3.47 | 1.55 | 0.36 | 4.22 | Wigner and Harland. |
| " Trinidad . . . . . . | 88.00 | 5.14 | 1.67 | 0.96 | 4.23 | Wigner and Harland. |
| " Porto Rico . . . . . | 87.50 | 4.84 | 2.60 | 0.81 | 4.25 | Wigner and Harland. |
| " St. Vincent . . . . . | 92.50 | 3.61 | 2.45 | 0.63 | 0.81 | Wigner and Harland. |
| " Demerara . . . . . . | 90.80 | 4.11 | 0.77 | 1.12 | 3.20 | Wallace. |
| " Benares . . . . . . . | 94.50 | 2.63 | 0.39 | 1.50 | 0.98 | Wigner and Harland. |
| " Unclayed Manila . . | 82.00 | 6.79 | 3.24 | 2.00 | 5.97 | Wigner and Harland. |
| " Concrete . . . . . . | 84.20 | 8.45 | 1.70 | 1.10 | 4.55 | Wallace. |
| " Melada . . . . . . . | 67.00 | 11.36 | 1.93 | 0.91 | 18.80 | Wallace. |
| " Bastards . . . . . . | 68.30 | 15.00 | 1.20 | 1.50 | 14.00 | Wallace. |
| Palm, East Indian . . . . . | 86.00 | 2.19 | 2.89 | 2.88 | 6.04 | Wigner and Harland. |
| Beet, First product . . . . | 94.17 | . . | 2.14 | 1.48 | 2.21 | Bodenbender. |
| " Second product . . . | 91.68 | . . | 2.49 | 2.92 | 2.91 | Bodenbender. |

2. REFINED SUGARS.—The commercial designations of refined sugar are very varied. We may distinguish in general between hard sugars and soft sugars, the former of which are more thoroughly and carefully dried by the aid of artificial heat, while the latter are merely centrifugated, and so retain from three to four per cent. of water in the traces of syrup adhering to the sugar. To the former class belongs sugar "crystals," or sugar in well-formed individual transparent crystals, which are as pure as rock-candy, as well as loaf-sugar in the forms of pulverized, crushed, granulated, and cube sugars. To the latter belong what are called grocery sugars, of which the finest grades are called A sugars, the next B sugars, and so on.

In Germany the finest white-beet-sugars are known as "raffinade," inferior grades as "melis" (or Brodzucker), as "pilé," and as "farin," the last of which is of inferior grain and color.

The hard sugars in general all show a sucrose percentage of ninety-nine or over, while the soft cane-sugars and the second grade beet-sugars show from ninety-six to ninety-eight per cent.

3. MOLASSES AND CANE-SUGAR SYRUPS.—The molasses may be termed the mother-liquor of the crystallized product, the sugar. It is never found possible in practice, however, to crystallize all the sugar out or to get a molasses which shall not contain sucrose. The potash salts, and in a lesser degree the calcium salts, which are present in the crude juice are "melassigenic,"—that is, prevent the crystallization of a certain amount of the sucrose; the invert sugar, or glucose, operates in the same way, and the long-continued heating of the sugar solutions also has the effect of increasing the molasses. In France, for instance, the *rendement*, or amount of crystallized sugar obtainable in refining of raw sugars, is calculated by deducting from the total sucrose twice the glucose, and from three to five times the ash. In the case of cane-sugars the ash is not so melassigenic, not being so largely composed of potassium compounds as with the beet, and a deduction of one and a half times the glucose is considered sufficient to allow for that impurity.

The experience of the last few years with sorghum-sugar, as manufactured by the United States Bureau of Agriculture and several sorghum-sugar factories in Kansas, has shown that this rule does not apply to sorghum. Professor Swenson, the chemist of the Parkinson Company at Fort Scott, Kansas, finds that in the case of sorghum juice the glucose and other solids, known as "non-sugar," prevent only two-fifths of their weight

of cane-sugar from crystallizing, so that in the season of 1887, instead of there being only 61.6 pounds available sugar per ton of cane worked as the analyses indicated according to the old rule, as a matter of fact, 130.5 pounds were obtained.

But with the sugar-cane and the sugar-beet the percentage of sucrose, in both the raw molasses produced in the extraction of the sugar from the juice and "refined molasses," the syrup produced in the process of refining is quite large. The composition of the first, second, and third molasses of the Louisiana cane-sugar plantation has already been given (see p. 145), as well as the average composition of beet-root molasses. The following analysis of a variety of molasses will further illustrate the differences in the several grades:

| | Sucrose. | Glucose. | Ash. | Organic non-sugar. | Water. | Authority. |
|---|---|---|---|---|---|---|
| *From sugar-cane:* | | | | | | |
| Green syrup | 62.7 | 8.0 | 1.0 | 0.6 | 27.7 | Wallace. |
| Golden syrup | 39.6 | 33.0 | 2.5 | 2.8 | 22.7 | Wallace. |
| Treacle | 32.5 | 37.2 | 3.5 | 3.5 | 23.4 | Wallace. |
| West Indian molasses | 47.0 | 20.4 | 2.6 | 2.7 | 27.3 | Wallace. |
| Dark molasses | 35.0 | 10.0 | 5.0 | 10.0 | 20.0 | J. H. Tucker. |
| *From beets:* | | | | | | |
| Beet-sugar molasses | 46.7 | 0.6 | 13.2 | 15.8 | 23.7 | Wallace. |
| Beet-sugar molasses | 50.0 | . . | 10.0 | 20.0 | 20.0 | Wigner and Harland. |
| Beet-sugar molasses | 55.0 | Trace. | 12.0 | 13.0 | 20.0 | J. H. Tucker. |

It will be seen from these analyses that the percentage of sucrose is usually much higher in the beet-root molasses, which is explained by the large percentage of ash and organic non-sugar. On the other hand, the glucose, or invert sugar, is large in the cane-sugar molasses, but almost entirely wanting in the beet-sugar molasses. The latter, however, always contains *raffinose*, another variety of sugar always present in the beet juice, *betäine*, a nitrogenous base, and proteids. The proportion of salts contained in beet-root molasses is usually ten to fourteen per cent., whereas refiner's molasses from cane-sugar rarely contains half that proportion.

The term *green syrup*, used above, is given to the syrup centrifugated from the second products in the refining process.

*Golden syrup* is produced from a refiner's molasses by diluting, filtering through bone-black, and then concentrating.

*Treacle* is the name formerly given to the drainings from the dark molasses sugars called bastards. (See p. 152.)

Cane-sugar molasses, when refined and brought to the condition of light-colored syrups, forms a common article of domestic consumption under the general name of table syrup. The table syrups of the present day, however, cannot, as a rule, claim to be simple products of the refining process, as they are almost always largely admixed with the cheaper glucose syrup, and the cane-sugar product in them is often entirely replaced by this latter. A glucose product, known as "mixing syrup," is quite openly sold for this purpose.

Beet-sugar molasses is not adapted for use as table syrup on account of the unpleasant taste and odor, due to the nitrogenous principles present. It is, as before described, worked for the extraction of the sugar, or it is fermented for alcohol.

4. Miscellaneous Side-products.—(1) *Exhausted Residue from the*

*Sugar-cane or Sugar-beet.*—The character of this residue differs very greatly according to the method of juice extraction which has been followed. The common sugar-cane residue from the roll-mills, known as "bagasse," consists of the fibre and cellular material of the cane still enclosing some six per cent. of sucrose, or about one-third of the total eighteen per cent. which the fresh-cut cane contains. It is very largely used as fuel on the sugar plantations, and the ash serves to some extent as fertilizing material for the soil. The cane-fibre, when freed more fully from the sugar by the diffusion process, has been proposed as a source of paper-stock. (See p. 128.)

Both the pressed pulp and the exhausted diffusion-chips from the sugar-beet are recognized as valuable cattle food. Märcker found in the dried press-cake 1.227 per cent. of nitrogen. The exhausted chips of the diffusion-cells are still richer in nitrogen, as the diffusion process does not extract as much nitrogenous matter as the method of crushing.

(2) *Scums and Saturation Press-cakes.*—In describing the production of raw cane-sugar mention was made of the scums, which had at one time been thrown away, but which when filter-pressed yielded a very considerable additional amount of sugar. The press-cake obtained in this treatment has also a value. It contains on an average as taken from the press 45.17 per cent. of water, 15.67 per cent. of ash, 3.49 per cent. of phosphoric anhydride, and 1.14 per cent. of nitrogen, or, reckoned on the dry material, 28.56 per cent. of ash, 6.33 per cent. of phosphoric anhydride, and 2.10 per cent. of nitrogen. Its value, as taken from the press, at the ruling rates for fertilizing materials, would be $10.64 per ton.* Where the carbonatation process is used, and the excess of lime removed by carbon dioxide, the scums and carbonate of lime are found together in the press-cake gotten by filtering. In the experimental tests of the carbonatation process as applied to cane-sugar made by the United States Department of Agriculture at Fort Scott, Kansas, in 1886,† the press-cake obtained after saturation and filtering when dried was found to contain 9.585 per cent. of albuminoids and 17.45 per cent. of other organic matter. The saturation press-cake of the beet-sugar process does not contain so high a percentage of albuminoids, but a much larger amount of nitrogenous compounds remains in the clarified juice, giving rise to the escape of ammonia on concentration in the vacuum-pan and showing itself in the molasses.

(3) *Exhausted Bone-black.*—The bone-black after repeated revivifying (see p. 150) becomes at last valueless for filtration purposes and passes out of the sugar-refinery, going to the manufacturer of fertilizers, for whom it is a very valuable material. The more calcium phosphate and the less calcium carbonate it contains, the more valuable it is for superphosphate manufacture, as, on the addition of sulphuric acid, the liberated phosphoric acid remains, adding to the value of the product, while the carbonic acid is driven off. The exhausted bone-black contains on an average thirteen per cent. of calcium carbonate, sixty to seventy-four per cent. of calcium phosphate, four per cent. of carbon, and four-tenths to six-tenths per cent. of nitrogen.

(4) *Vinasse, or Molasses Residues.*—When the beet molasses is fermented for the production of alcohol, the residual liquor, which contains all the potash salts of the molasses, is known in French as "vinasse," or in German as "schlempe." It is of about 41° B. and acid in reaction. It is neutral-

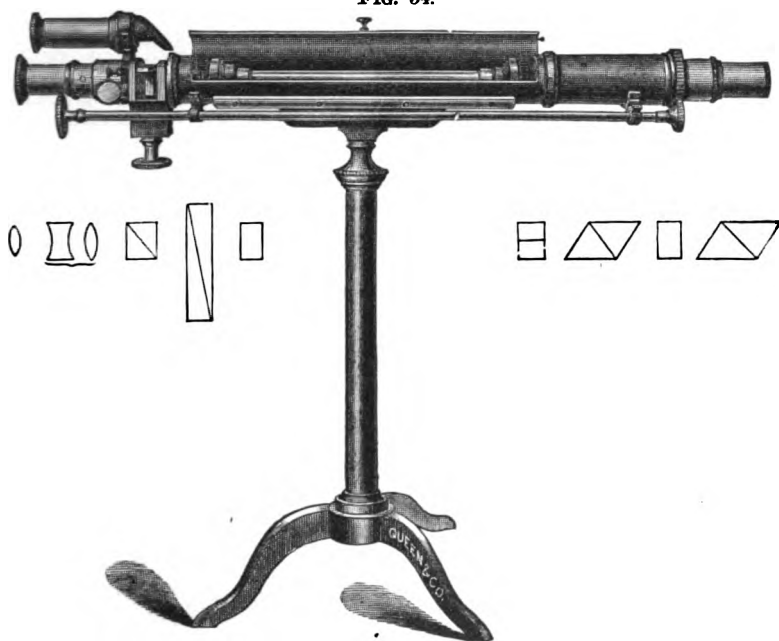
* Bulletin of Department of Agriculture, No. 11, p. 16.
† Ibid., No. 14, p. 54.

ized with calcium carbonate and then evaporated down to dryness and calcined. The black porous residue so obtained contains thirty to thirty-five per cent. of potassium carbonate, eighteen to twenty per cent. of sodium carbonate, eighteen to twenty-two per cent. of potassium chloride, six to eight per cent. of potassium sulphate, and fifteen to twenty-eight per cent. of insoluble matter. It is exhausted with hot water, and the extract evaporated down, when potassium sulphate and afterwards sodium carbonate separate out. On cooling, potassium chloride and potassium sulphate crystallize out, and the mother-liquor contains potassium carbonate admixed with some sodium carbonate. It is possible by this gradual evaporation and fractional crystallization to bring the crude potashes to a purity of ninety per cent. In this production of the solid potashes from the molasses residue all the nitrogen of the molasses is lost. To prevent this, C. Vincent, a French chemist, has proposed to submit the evaporated vinasse to a dry distillation instead of calcination in the air. The residue of this distillation is an open and very porous coke containing all the mineral salts of the molasses, which can then be extracted as before. The products of distillation are an illuminating and heating gas, ammonia water, and a small amount of tar. The ammonia water is the most interesting product. It contains besides carbonate, sulphide and cyanide of ammonium, methyl alcohol, and notable quantities of trimethylamine. This latter can be decomposed at 320° C. by dry hydrochloric acid gas into methyl chloride and ammonia, and on passing the products through aqueous hydrochloric acid, the methyl chloride goes through unabsorbed, while the ammonia is taken up. The methyl chloride is of great value for ice machines and for the manufacture of methylated aniline colors. (See p. 412.) The process was quite largely introduced, but as in recent years the molasses is worked over for sugar in increasing amounts, less molasses is fermented, and hence less vinasse is obtained.

## IV. Analytical Tests and Methods.

1. Determination of Sucrose.—(*A*) *Optical Methods.*—Among the most important physical properties of many of the varieties of sugars is the power possessed by their solutions of rotating the plane of polarization to the right or the left. They are accordingly classified as dextro-rotatory, lævo-rotatory, or optically inactive in case no power of circular polarization is manifested. This property as possessed by solutions of cane-sugar, of deviating the polarized ray in a fixed and definite degree, has been made the basis of the method of analysis by means of polariscopes. The fundamental idea involved in these instruments is to compensate for and so determine the optical rotatory power of sugar solutions of unknown strength by the corresponding circular polarizing action of quartz plates of known thickness, and hence of known power. The earliest of polariscopes was the Mitscherlich instrument, but those now in use for sugar analysis are either the Soleil-Ventzke-Scheibler, the Soleil-Dubosq, the Laurent shadow instrument, or the Schmidt and Haensch, which last claims to combine the best features of the Soleil and the Laurent instruments. A general view and a longitudinal section of this instrument is given in Fig. 54. The glass tube containing the sugar solution is shown lying in the axis of the telescope and the polarizing prisms. To the right below is shown the polarizing prism (the so-called Jellet-Cornu prism), to the left is the analyzing prism, a quartz plate, quartz wedges of opposite rotatory power, and the lenses

of the telescope, with a plate of bichromate of potash to correct for any color in the field. In this instrument, which uses white light, the field of view is a circle, which, with the instrument at 0° and nothing intercepting the light, is of a uniform gray tint. When a sugar solution is interposed, one-half of the circle becomes darker than the other, and the quartz wedges, controlled by the screw shown underneath, must be moved to compensate for the rotation due to the sugar solution and to restore the uniformity of tint. The instrument is so graduated that one degree of displacement on the scale corresponds to .26048 gramme of cane-sugar dissolved in 100 cubic centimetres of water and viewed through a 200-millimetre tube. Therefore 26.048 grammes of the sugar to be analyzed are weighed out. If chemically pure and anhydrous, the solution of the strength stated should read one hundred

FIG. 54.

degrees of displacement, or one hundred per cent. of sugar, and if impure, correspondingly less.

In the application of polariscope analysis to cane-sugars two cases may arise: first, when no other optically active substance is present, and, second, when glucose or invert sugar is also present.

(*a*) *Absence of other Optically Active Substances.*—The weighed sample is dissolved in about fifty cubic centimetres of water in a flask marked for one hundred cubic centimetres. As soon as the sugar is all dissolved, a few cubic centimetres of a solution of basic acetate of lead are added, and two or three cubic centimetres of cream of hydrated alumina. The liquid is well agitated, and then the flask is filled nearly to the mark on the neck with water and the froth allowed to rise to the surface, when it is flattened by the addition of a drop of ether. Water is now added exactly to the mark, the contents of the flask thoroughly agitated, and the liquid filtered through a dry filter. In the case of very dark sugars, purified and perfectly dry bone-

black has been added for clarifying purposes. However, it is generally acknowledged to introduce error by its absorption of small amounts of sugar, so that it is now dispensed with, or if used on the dry filter, the first third of the filtrate is rejected and the later portions only used. Allen * recommends instead the use of a ten per cent. solution of sodium sulphite. The tube of the polariscope is now rinsed with the clear sugar solution and then filled with the same, the open end closed with a smooth glass plate held in place by a brass cap, which is screwed on. The tube containing the sugar solution is then placed in the instrument, and the lower thumb-screw turned until the uniformity of shade in the two halves of the field is restored, when the number of degrees (or percentage of cane-sugar in the sample) is read off on the scale.

(*b*) *Presence of Glucose, Invert Sugar, or other Optically Active Substance.*—The action of acids upon cane-sugar has already been stated to cause inversion,—*i.e.*, change of the sucrose into dextrose and levulose. Both these varieties of sugars differ from sucrose in their optical power. If, then, these alteration products accompany the sucrose in a cane-sugar sample, the results of the polariscope reading may be vitiated. Some writers have held that the invert sugar present in raw cane-sugars and syrups is optically inactive, but the statement seems to have been disproved by Meissl. Besides, in raw beet-sugars and syrups, raffinose, a very strong dextro-rotatory sugar, is found vitiating the readings for cane-sugar. The correction of the original polarization in such cases is most generally made by the method of inversion proposed by Clerget. The direct polarization is taken in the usual way, and a part of the solution remaining from the one hundred cubic centimetres prepared for this test is put into a 50-cubic-centimetre flask, which has also a 55-cubic-centimetre mark on the neck. Fifty cubic centimetres having been taken, five cubic centimetres of concentrated hydrochloric acid is added, and the whole heated on a water-bath to 70° C. for some ten minutes. This suffices to completely invert the cane-sugar present, while the original invert sugar is unacted on. The flask is then cooled, and part of the liquid is filled into a 220-millimetre tube, closed by glass plates at both ends and provided with a tubulure in the side so that a thermometer may hang suspended in the liquid when the observation is made. The reading will generally be much reduced from the original dextro-rotatory reading, and may even be some degrees to the left. If, then, $S$ represent the sum or difference of polariscope readings before and after inversion (difference if both are to the right, sum if the second reading is to the left), $T$ the temperature of the inverted solution when polarized, and $R$ the correct percentage sought, $R = \frac{200\,S}{285 - T}$. Clerget has also prepared an elaborate set of tables which make the use of the formula unnecessary. (See also under molasses, p. 162.)

(*B*) *Chemical Methods.*—The only chemical method for the determination of cane-sugar ever resorted to is the inversion of the cane-sugar, neutralizing with sodium carbonate, and determination of the reducing sugar so obtained by the method to be described under the next head. The inversion takes place in definite proportions, so that nineteen parts of sucrose produce twenty parts of the invert sugar. When invert sugar is also present in the solution

* Commercial Organic Analysis, 3d ed., vol. i. p. 257.

of which the cane-sugar is to be determined by inversion, the former is first estimated as a separate operation, and then a portion of the original solution is inverted, and the total invert sugar, including that formed from the cane-sugar, is determined.

2. DETERMINATION OF GLUCOSE, OR INVERT SUGAR.—The oldest method is that based on Trommer's reaction as applied to sugar analysis by Barreswill and Fehling. This depends upon the fact that an alkaline solution of copper oxide containing a fixed organic acid, as tartaric, is reduced with the separation out of insoluble cuprous oxide by dextrose, or invert sugar, while cane-sugar has no effect. The composition of a standard Fehling's solution, as it is called, is thus given by Tollens: * 34.639 grammes crystallized copper sulphate are dissolved in water and brought to 500 cubic centimetres; 173 grammes Rochelle salt and 60 grammes sodium hydrate are also dissolved in water and brought to 500 cubic centimetres. Equal volumes of these solutions are mixed when required for use and constitute the correct Fehling's solution. The ready-prepared Fehling's solution changes in the course of some days in effective power even when kept in a cool place and in the dark. Ten cubic centimetres of the Fehling's solution given above correspond to .05 gramme dextrose, or invert sugar, or .0475 gramme cane-sugar made active by inversion. For technical determinations merely the work with the solution can be volumetric; for more exact scientific purposes it must be gravimetric, weighing the copper as metal or as cupric oxide. In carrying out the volumetric test, the sugar solution in which glucose is to be determined is placed in a burette. If dark, it may be previously cleared with a small quantity of bone-black, or if it be some of the solution prepared for polarization, it is prepared without lead solution, an aliquot portion taken out for this glucose determination, and the remainder treated with a measured quantity of the lead solution, for which allowance is made. Any lead in this glucose solution must be eliminated thoroughly. This is best done with sulphurous acid, the change of strength in the liquid being noted. Ten cubic centimetres of the mixed Fehling's solution are now measured into a porcelain dish, diluted with twenty or thirty cubic centimetres of water and brought quickly to boiling, when the sugar solution is run in two cubic centimetres at a time, boiling between each addition. When the blue color has nearly disappeared the sugar solution should be added, in small amount but still rapidly. The end of the reaction is reached when a few drops of the supernatant liquid filtered into a mixture of acetic acid and dilute potassium ferrocyanide give no brown color.

In carrying out the gravimetric method the Fehling's solution remains in excess, while the precipitated cuprous oxide is carefully filtered off and further treated. The procedure is as follows: Sixty cubic centimetres of the mixed Fehling's solution and thirty cubic centimetres of water are boiled up in a beaker glass, twenty-five cubic centimetres of the dextrose solution of approximately one per cent. strength added, and the mixture again boiled. It is then filtered with the aid of a filter-pump upon a Soxhlet filter (asbestos layer in a tared funnel of narrow cylinder shape), quickly washed with hot water, and then with alcohol and ether, and dried. The asbestos filter, with the cuprous oxide, are now heated with a small flame, while a current of hydrogen is passed into the funnel, so that the precipitate

* Handbuch der Kohlenhydrate, 1888, p. 71.

is reduced to metallic copper. It is allowed to cool in the current of hydrogen, placed for a few minutes over sulphuric acid, and then weighed. A table has been constructed by Allihn which gives in milligrammes the dextrose corresponding to the weight of copper found.

Other methods for the determination of dextrose are those of Pavy, using an ammoniacal solution of the Fehling reagent; of Knapp, who uses an alkaline solution of cyanide of mercury; of Sachsse, who uses an alkaline solution of potassio-mercuric iodide; and of Soldaini, who uses a solution of basic carbonate of copper dissolved in potassium bicarbonate. This last reagent has been recently strongly commended as better than Fehling's solution, in that it is more sensitive to glucose and is much less affected by cane-sugar even after prolonged boiling.*

3. ANALYSIS OF COMMERCIAL RAW SUGARS.—Raw sugars contain, besides the cane-sugar, invert sugar, moisture, mineral salts, organic non-sugar, and insoluble matter. Raw beet-sugars contain, in addition to the sucrose and glucose just mentioned, small quantities of raffinose, a variety of sugar found in the beet juice and present in all the products from it.

The cane-sugar present is partly crystallized and partly uncrystallizable. Both are, of course, counted together in the polarization figures, but only the first is capable of extraction in the refining process. The method of estimating the crystallized cane-sugar for itself will be described later on. The polarization methods have already been described. In raw sugars containing much invert sugar, such as those from the cane, the double polarization (before and after inversion) is alone to be relied upon.

The methods for glucose have also been described.

The determination of moisture is made by taking five grammes of the sample and drying it spread out on a weighed watch-crystal in an air-bath at 100° to 110° C. until it ceases to lose weight. As sugars containing much glucose cannot stand the heat without some alteration, in their case a lower temperature (60° to 90° C.) is used. For very syrupy sugars and melados it becomes necessary to dry with the addition of a weighed amount of clean sand. Drying in a vacuum is also practised in many cases, as the operation is shortened and less risk of alteration exists.

The mineral salts are determined as ash. The following analyses give the average composition of raw cane- and beet-sugar ash according to Monier:

| | Cane-sugar. | Beet-sugar. |
|---|---|---|
| Potassium (and sodium) carbonate | 16.5 | 82.2 |
| Calcium carbonate | 49.0 | 6.7 |
| Potassium (and sodium) sulphate | 16.0 | 11.1 (with sodium chloride) |
| Sodium chloride | 9.0 | |
| Silica and alumina | 9.5 | None. |
| | 100.0 | 100.0 |

Owing to this decided difference, it is much easier to get the ash of cane-sugars completely burned and in weighable condition than that of beet-sugars, which contain so much of the deliquescent and alkaline carbonates. To obviate this difficulty, Scheibler proposes to treat the sugar with sulphuric acid before igniting it, by which means the ash obtained contains the bases as non-volatile, difficultly fusible and non-deliquescent sulphates instead of as carbonates. A deduction of one-tenth of the weight of the sulphated ash must be made in this case for the increase due to the sulphuric acid.

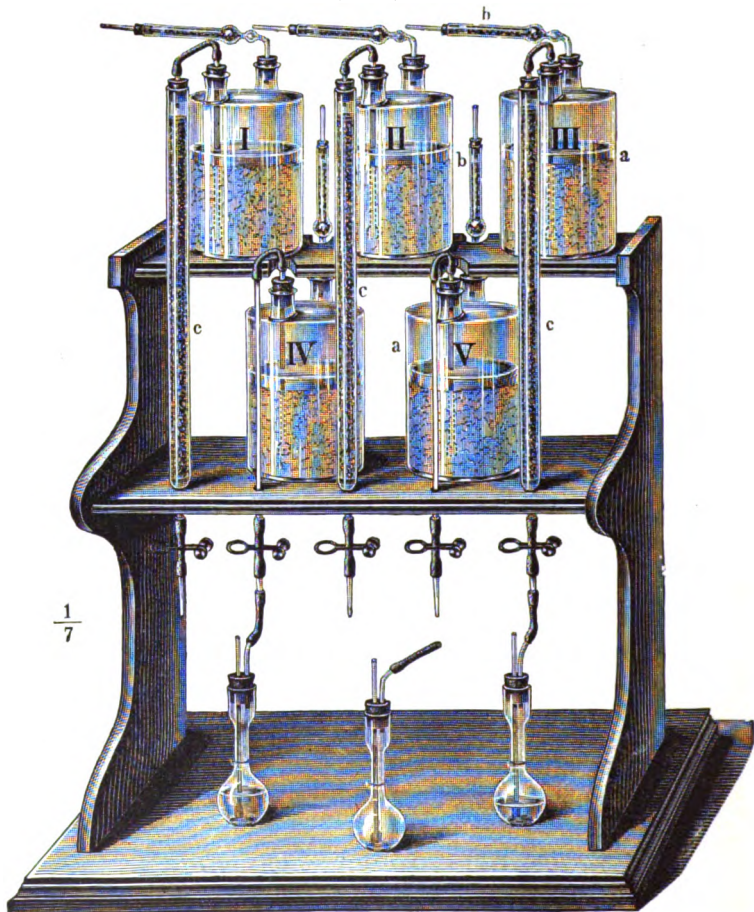
* Bodenbender and Scheller, Zeitschrift für Rübenzucker, 1887, p. 138

The soluble and insoluble ash are often distinguished in addition to total ash. In ordinary commercial analyses of sugars, the sum of the cane-sugar, glucose, ash, and water is subtracted from one hundred, and the difference called organic or undetermined matters. This would include both the soluble organic impurities and the insoluble impurities, such as fibre and particles of cane. Two processes have been proposed for determining the soluble organic impurities separately: Walkoff's method of precipitation with tannin, and the basic acetate of lead method. Neither method is in very general use.

As before stated, the full analysis of a raw sugar will not give any exact measure of its refining value,—that is, of the amount of crystallized cane-sugar that can be extracted from it. The so-called method of coefficients adopted in France, whereby five times the ash, plus once or twice the glucose percentage subtracted from the cane-sugar percentage, is taken to represent the crystallized cane-sugar obtainable, is not much to be depended upon. The true refining value, or *rendement*, of a raw sugar can, however, be determined by a special procedure first proposed by Payen and afterwards improved by Scheibler. The process depends upon the fact that if raw sugars be treated with a saturated alcoholic solution of cane-sugar acidified with acetic acid, the coloring matter and other impurities, together with the syrup and other uncrystallizable constituents, are removed, while the crystallized sugar remains unchanged. The sugary alcoholic liquids are then displaced by absolute alcohol. Fig. 55 shows the arrangement of vessels. The bottle I contains eighty-five per cent. alcohol, to which 50 cubic centimetres of acetic acid is added per litre, and the mixture allowed to stand in contact with an excess of powdered white sugar for a day, being shaken at intervals; bottle II, alcohol of ninety-two per cent. saturated as the other, but without acetic acid; bottle III, alcohol of ninety-six per cent., also saturated with sugar; and bottle IV, a mixture of two-thirds absolute alcohol and one-third ether. Of the sugars to be examined, weights are taken corresponding to the polariscope used, placed in the upright tubes, washed with the successive solutions, and dried by the aid of a filter-pump ready for use in the polariscope test. In carrying out the process, the alcohol and ether mixture is first run in that it may take up any moisture and throw out the sugar that such moisture may have dissolved, then successively down to No. I, which is the effective washing solution. This is then displaced by Nos. II, III, and IV in succession. The method is thoroughly reliable, but great care must be taken to keep the alcoholic solutions just saturated with sugar through all changes of temperature.

4. ANALYSES OF MOLASSES AND SYRUPS.—The composition of both the cane-sugar and the beet-sugar molasses have already been given (see p. 154), and it was seen that they differed notably. Both still contain considerable quantities of sucrose, but for different reasons. With the cane-sugar molasses because of the invert sugar, with the beet-sugar molasses because of the melassigenic salts. In either case the polariscope reading for sucrose must be corrected by inversion. The glucose is determined as described under raw sugars. The water is determined by weighing out a sample, thinning it with water, putting it into a weighed dish with clean sand, and drying it at a temperature of 60° C. until constant. Drying in a partial vacuum also facilitates the drying off of the moisture. The ash is determined as with raw sugars, sulphuric acid being added, and the bases

weighed as sulphates instead of as carbonates, the proper correction being made. The organic non-sugar is simply taken by difference as with raw sugars. The determination of raffinose in raw beet-sugars, and particularly in beet-molasses, has attracted much attention in recent years. Creydt* has suggested a way for determining it in the presence of cane-sugar in connection with the method of inversion. He finds that while cane-sugar polarizing 100° to the right before inversion polarizes 32° to the left after inversion, a change of 132°, raffinose changes from 100° to 50.7°

FIG. 55.

only, a change of 49.3°. He proposes two formulas: $A = z + 1.57\ R$, and $c = 1.322 + 1.57\ R \times .493$, in which $A$ is the direct polarization, $c$ the polarization after inversion, $z$ the percentage of cane-sugar, and $R$ that of raffinose. From these formulas, $A$ and $c$ being known, $z$ and $R$ can be found. The reading after inversion must be taken uniformly at 20° C.

5. ANALYSES OF SUGAR-CANES AND SUGAR-BEETS AND RAW JUICES THEREFROM.—The very different physical characters of the sugar-

* Zeitschrift für Rübenzucker, vol. xxxvii. p. 163.

cane and the sugar-beet, the one a bamboo-like shell enclosing a woody pith, and the other a soft root easily brought into pulpy consistency, make the work upon them quite different. In the case of the cane, the samples to be analyzed are weighed and then pressed between rolls, moistened with hot water and again pressed, and this repeated several times. The exhausted stalk, or "bagasse," is usually not further examined, but in the juice the sucrose, glucose, ash, and organic non-sugar are determined as before described. In all analyses of raw cane juices the percentage of total solids is determined by the Brix saccharometer or "spindle." The form of hydrometer in most general use is known as the Balling or Brix, and its readings indicate directly the percentage of impure sugar or solid matter dissolved. Sets of tables also allow of the conversion of the Brix scale into direct specific gravity figures. (See Appendix, p. 515.) With the aid of the specific gravity determination it is possible to make a rapid analysis of raw juice without weighing. The method adopted by Crampton,* one of the chemists of the United States Bureau of Agriculture, for this analysis is to measure out a certain volume of the juice, add lead solution, make up to another definite volume, polarize, and apply the correction for specific gravity to the reading obtained. A set of tables for this correction and the factor needed in the glucose determination are given by Crampton.

In the examination of sugar-beets, the system of pressing and moistening with hot water can be followed for the extraction of the juice, but the method proposed by Scheibler of extracting the sugar from a weighed quantity of the pulp by the aid of alcohol is much better. This is accomplished by the aid of a Soxhlet or other extractor (see p. 78) connected with an upright condenser. After complete extraction and cooling the necessary amount of lead solution is added, and the liquid brought up to the mark with absolute alcohol and then polarized. Degener has described a still simpler form of extraction, originally suggested by Rapp, in which the pulp remains in the alcoholic solution until after it is cleared with the lead solution and brought to the mark, when it is filtered and polarized. A correction must in this case be applied to the reading on account of the volume occupied by the pulp in the measured liquid.

The amount of dry residue, or "mark," of the beet can be determined in the Scheibler extraction method at the same time by taking the exhausted residue, drying it in a current of air, and weighing it. The moisture and ash of the beet are determined as with raw sugars. The organic non-sugar is gotten by difference or by one of the methods mentioned under raw sugars

6. Analyses of Side-products.—(*a*) *Of Bone-black.*—Careful analyses of both fresh char and that which is in use are needed to allow of the proper control in filtration. The most important determinations are those of water, carbonate of lime, carbon, and specific gravity, as upon the changes in these depend in the main its efficiency. The water is determined by drying for several hours at 140° C. The sample should not be powdered. The carbon is determined by treating a weighed quantity of the char with pure hydrochloric acid, with the aid of heat, on a water-bath until the soluble portions have been dissolved, diluting and filtering upon a weighed quantitative filter. After thorough washing with hot water, the filter and contents are dried at 100°, placed between watch-glasses and weighed, again heated and weighed as long as any loss of weight is shown. The filter and carbon

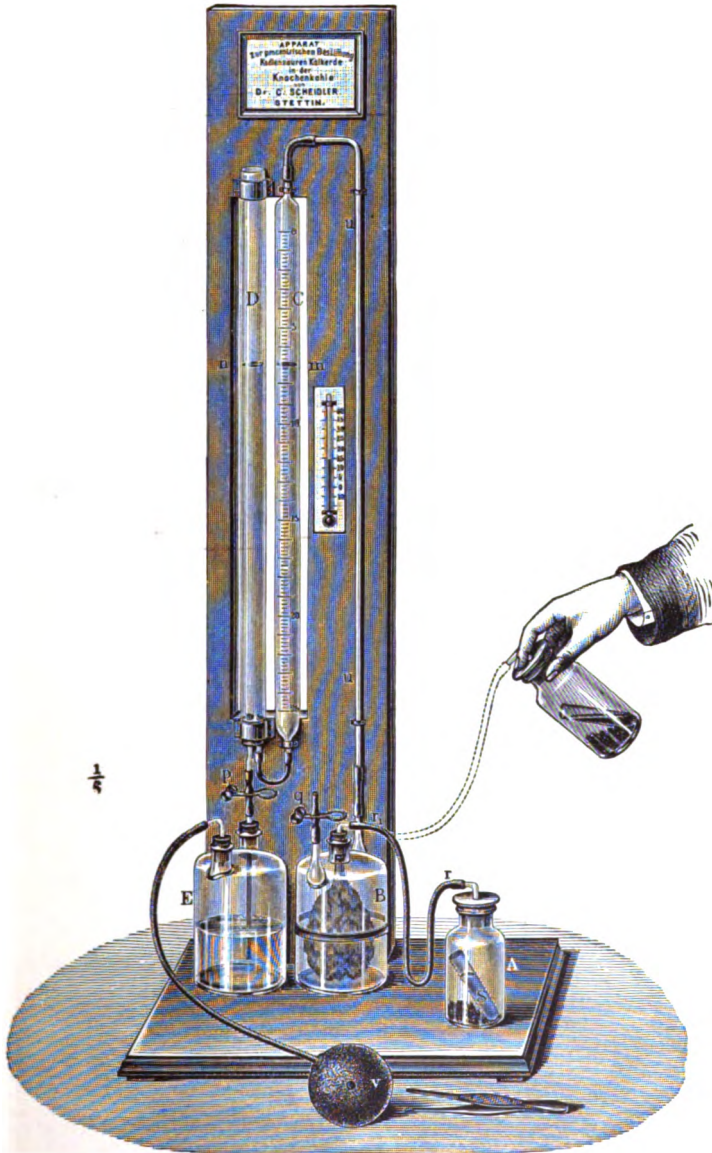
* United States Bureau of Agriculture, Bulletin No. 15, pp. 31–35.

are then transferred to a weighed crucible and ignited. The insoluble residue, taken from the previous weight, minus the weight of the filter, gives the amount of carbon. The estimation of carbonate of lime in case the char is used with cane-sugar or juices is of much less importance than when the char is used with beet-sugars or juices. In the former case, the percentage decreases at first, and then remains nearly stationary, in the repeated use of the char, while in the latter case it would increase steadily, because of the more thorough liming and carbonatation to which the beet juices are subjected, were it not for the treatment with hydrochloric acid in the revivifying of the char. (See p. 150.) To allow of the proper judgment in this use of hydrochloric acid, it becomes necessary in beet-sugar working to determine carefully the amount of carbonate of lime taken up by the char in using before starting the revivification. It is almost universally done at present by the aid of the Scheibler apparatus, shown in Fig. 56. The normal quantity of pulverized char (1.702 grammes) is placed in *A*, and the tube *S* filled with acid to the mark is carefully placed in the bottle. *E* is then filled with water, and the operator, by means of the compression-bulb, forces the liquid into *D* and *C*, which connect at the base, until it reaches a little above the zero-point in *C*, when it is allowed to flow out by opening the pinchcock at *p* until the level in *C* is at zero. The stopper now being placed in *A*, a connection with *B* is made by the tube *r*. If the level of the liquid in *D* and *C* are then unequal, the equality may be restored by opening the cock *q* for a few seconds, and which for the rest of the operation remains closed. The vessel *A* is now held, as shown in the cut, so that the acid may come in contact with the char, and the bottle gently shaken to cause the acid to thoroughly mix with the assay. The pressure of the gas evolved distends the rubber bag in *B* and depresses the column of water in *C*. The stopcock *p* is now opened to allow the water in *D* to flow out sufficiently rapidly to keep the level in *C* and *D* as near the same as possible during the progress of the determination. When all the gas has been given off and the level of the liquid in *C* becomes stationary, *p* is closed, after bringing the water in *D* to the same level as that in *C*, and the volume and temperature read off. A set of tables accompanying the instrument gives the percentage of carbonate of lime from the volume and temperature readings. Assuming seven per cent. to be the normal amount of carbonate of lime in the char, any excess, as shown in this determination, can have its equivalent in hydrochloric acid of known strength calculated, and thus the acid treatment in the revivifying process can be made accurate.

In determining specific gravity, both apparent and real specific gravity (the latter after boiling the char with distilled water to displace air) are to be taken.

(*b*) *Of Scums, Press-cakes, and Sucrates.*—In the case of the scums and press-cakes obtained in the manufacture of raw sugars, their chief value is in the lime salts they contain, which, notably in the case of beet-sugars, adapt them for use as fertilizing materials. They, however, contain such amounts of sugar, either mechanically held, or, where the carbonatation process has been used, as sucrates, as make it necessary to regularly determine the sucrose in them. In the case of the thin scums from cane-sugar working, the determination can be made exactly as with an impure juice before described. In the case of the heavier press-cakes from beet-sugar working, resulting from carbonatation, the procedure is different. Here the sucrate of lime is to be decomposed if possible without decomposing the large amount of accompanying

carbonate of lime. This is done by careful addition of acetic acid, controlling the reaction with phenol-phthaleïn. For details of this process, first proposed by Sidersky, see Frühling and Schultz, "Anleitung zür Zucker Untersuchungen," 3d ed., p. 171.

FIG. 56.

**Sucrates**, resulting from the working of molasses for sugar by either of the lime or strontium processes (see p. 147), are analyzed by a somewhat similar procedure, using strong acetic acid to set the sugar free from its combination with the lime or strontia and phenol-phthaleïn as an indicator.

The excess of acid is afterwards neutralized, lead solution added, the solution brought to strength, and polarized. (Ibid., p. 155.)

## V. Bibliography and Statistics.

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### STATISTICS.

1. PRODUCTION OF SUGAR FROM THE CANE.—The total production of raw sugar from the sugar-cane for the last two years is thus estimated by Willet and Gray:

| | 1898–99. Tons. | 1899–1900 (estimated). Tons. |
|---|---|---|
| Cuba | 345,261 | 440,000 |
| Porto Rico | 53,825 | 50,000 |
| Louisiana | 224,000 | 132,000 |
| Trinidad (export) | 53,436 | 45,000 |
| Barbadoes (export) | 42,000 | 35,000 |
| Guadeloupe | 40,000 | 30,000 |
| Hayti and St. Domingo | 50,000 | 55,000 |
| Other West Indies | 103,000 | 104,000 |
| Mexico and Central America | 22,000 | 24,000 |
| Demerara and Surinam | 81,000 | 81,000 |
| Peru (export) | 110,000 | 100,000 |
| Argentine Republic | 80,000 | 90,000 |
| Brazil | 151,495 | 160,000 |
| British India (export) | 10,000 | 10,000 |

| | 1898–99. Tons. | 1899–1900 (estimated). Tons. |
|---|---|---|
| Siam | 7,000 | 7,000 |
| Java (export) | 689,281 | 650,000 |
| Philippines | 76,000 | 70,000 |
| Australia and Polynesia | 228,734 | 215,000 |
| Hawaii | 252,506 | 275,000 |
| Egypt | 90,000 | 80,000 |
| Mauritius, etc. | 186,487 | 160,000 |
| Réunion, etc. | 37,781 | 35,000 |
| Spain | 8,000 | 8,000 |
| | 2,941,806 | 2,856,000 |

2. PRODUCTION FROM THE SUGAR-BEET.—The world's production of beet-sugar for the last four years has been as follows:

| | 1895–96. | 1896–97. | 1897–98. | 1898–99. |
|---|---|---|---|---|
| | Metric tons. | Metric tons. | Metric tons. | Metric tons. |
| Germany | 1,617,812 | 1,836,536 | 1,847,018 | 1,700,000 |
| Austria-Hungary | 781,000 | 934,000 | 831,600 | 896,000 |
| France | 653,097 | 735,367 | 808,006 | 725,000 |
| Russia | 775,000 | 730,000 | 735,000 | 745,000 |
| Belgium | 225,000 | 290,000 | 225,000 | 210,000 |
| Holland | 105,000 | 175,000 | 125,000 | 155,000 |
| Other countries | 150,000 | 200,000 | 283,000 | 250,000 |
| Total | 4,306,909 | 4,900,903 | 4,854,624 | 4,681,000 |

3. IMPORTATIONS OF SUGAR INTO THE UNITED STATES.—The total importations of sugar (raw and refined) during the last few years have been:

| | | | |
|---|---|---|---|
| 1897 | 4,101,211,595 pounds, | valued at | $81,729,142 |
| 1898 | 3,427,260,146 " | " | 77,934,097 |
| 1899 | 4,399,748,654 " | " | 108,124,877 |

Of this, the amount of raw sugar was as follows:

| Beet-sugar. | | Cane-sugar. | |
|---|---|---|---|
| 1897 | 1,373,230,362 lbs. | 1897 | 2,541,386,927 lbs. |
| Valued at | $24,181,704 | Valued at | $53,084,357 |
| 1898 | 418,981,330 lbs. | 1898 | 2,930,567,531 lbs. |
| Valued at | $8,422,020 | Valued at | $67,584,076 |
| 1899 | 592,363,918 lbs. | 1899 | 3,775,340,352 lbs. |
| Valued at | $12,839,458 | Valued at | $94,298,311 |

4. PRODUCTION AND CONSUMPTION OF SUGAR IN THE UNITED STATES DURING RECENT YEARS.

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| | Tons. | Tons. | Tons. | Tons. |
| Refined from imported sugar | 1,670,963 | 1,715,607 | 1,708,937 | 1,844,642 |
| Manufactured from imported molasses | 603 | 150 | 1,700 | 5,200 |
| Cane-sugar produced | 243,220 | 310,537 | 252,812 | 160,400 |
| Beet-sugar " | 40,000 | 39,684 | 34,453 | 79,368 |
| Maple-sugar " | 5,000 | 5,000 | 5,000 | 5,000 |
| Sorghum, etc. " | 300 | .... | .... | .... |
| Total sugar " | 1,960,086 | 2,070,978 | 2,002,902 | 2,094,610 |
| Consumption per capita | 61.6 lbs. | 63.7 lbs. | 60.3 lbs. | 61.7 lbs. |

# CHAPTER V.

## THE INDUSTRIES OF STARCH AND ITS ALTERATION PRODUCTS.

### I. Raw Materials.

STARCH is one of the most important, as well as most widely occurring, productions of the vegetable kingdom. It constitutes, either when extracted from vegetable raw materials, or more generally in admixture with the other plant constituents, the staple article of food for the great bulk of the human race. It is only necessary to call attention to the fact that the principal cereal grains used throughout the world for food contain starch as their chief ingredient, and that the tubers of many plants and the stems and roots of some trees also yield starch in great abundance.

The most complete enumeration and classification of starches is that of Muter as amplified by Allen* and Blyth,† by which they are divided into five groups on the basis of their physical and microscopical differences, as follows:

I. *The potato group* includes such oval or ovate starches as give a play of colors when examined by polarized light and a selenite plate and having the hilum and concentric rings clearly visible. It includes *tout les mois*, or canna arrow-root, potato starch, maranta, or St. Vincent arrow-root, Natal arrow-root, and curcuma arrow-root.

II. *The leguminous starches* comprise such round or oval starches as give little or no color with polarized light, have concentric rings all but invisible, though becoming apparent in many cases on treating the starch with chromic acid, while the hilum is well marked and cracked, or stellate. It includes the starches of the bean, pea, and lentil.

III. *The wheat group* comprises those round or oval starches having both hilum and concentric rings invisible in the majority of granules. It includes the starches of wheat, barley, rye, chestnut, and acorn, and a variety of starches from medicinal plants, such as jalap, rhubarb, senega, etc.

IV. *The sago group* comprises those starches of which all the granules are truncated at one end. It includes sago, tapioca, and arum, together with the starch from belladonna, colchicum, scammony, podophyllum, canella, aconite, cassia, and cinnamon.

V. *The rice group.* In this group all the starches are angular or polygonal in form. It includes oats, rice, buckwheat, maize, dari, pepper, as well as ipecacuanha.

In addition to the differences in form and marking mentioned above, the starch-granules differ in size according to their different sources, so that under the microscope they can be distinguished by the measurement of the average diameter of the granule. This ranges, according to Karmarsch, from .01 to .185 millimetre, or from .0004 to .0079 inch.

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* Com. Org. Anal., 2d ed., vol. i. p. 335. † Blyth, Foods, Compos. and Anal., p. 139.

For practical purposes we may now speak of two classes only of these starch-containing materials,—viz., the cereals and the plants in which the starch is extracted from tubers, roots, or stems, such as potatoes on the one hand, and the West Indian starch preparations, like arrow-root, sago, and tapioca, on the other. As before stated, starch is the chief ingredient in the cereals, but not at all the only one. The composition of the more important cereals is thus given by Bell:*

| CONSTITUENTS. | Wheat. Winter sown. | Wheat. Spring sown. | Long-eared barley. | English oats. | Maize. | Rye. | Carolina rice (without husk). |
|---|---|---|---|---|---|---|---|
| Fat | 1.48 | 1.56 | 1.03 | 5.14 | 3.58 | 1.43 | 0.19 |
| Starch | 63.71 | 65.86 | 63.51 | 49.78 | 64.66 | 61.87 | 77.66 |
| Sugar (as sucrose) | 2.57 | 2.24 | 1.34 | 2.36 | 1.94 | 4.30 | 0.38 |
| Albumen (insoluble in alcohol) | 10.70 | 7.19 | 8.18 | 10.62 | 9.67 | 9.78 | 7.94 |
| Nitrogenous matter (soluble in alcohol) | 4.83 | 4.40 | 3.28 | 4.05 | 4.60 | 5.09 | 1.40 |
| Cellulose | 3.03 | 2.93 | 7.28 | 13.53 | 1.86 | 3.23 | Traces. |
| Mineral matter | 1.60 | 1.74 | 2.32 | 2.66 | 1.35 | 1.85 | 0.28 |
| Moisture | 12.08 | 14.08 | 13.06 | 11.86 | 12.34 | 12.45 | 12.15 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

The chemical formula of starch is $(C_6H_{10}O_5)_n$. According to Tollens, confirmed by Mylius, it is $C_{24}H_{40}O_{20}$; according to Brown soluble starch is $C_{120}H_{200}O_{100}$, while for the ordinary variety he proposes $C_{180}H_{300}O_{150}$. Nägeli stated that by subjecting the starch-granules to the slow action of saliva, salt solutions, and dilute acids two substances could be shown to be present, *granulose*, which dissolved, and *cellulose* (or, as it has been called, *farinose*), which remained. Arthur Meyer considers that there is only a single substance originally present, and that the cellulose, or farinose, which remains is a decomposition product of the starch.

Air-dried starch always retains from eighteen to twenty per cent. of water. It is soluble in cold water, alcohol, ether, ethereal and fatty oils. When it is heated with twelve to fifteen times its bulk of water to 55° C., it begins to show signs of change, swelling up, and at a temperature of from 70° to 80° C. (or even below 70° C. with some pure starches) the granules burst and it becomes a uniform translucent mass, known as "starch-paste," which is not, however, a solution, as the water can be frozen out of it. Boiled with water for a long time it goes into solution, one part dissolving in fifty parts of water. The action of heat upon starch is to change it gradually into *dextrine*, which is soluble in cold water.

One of the best known of the reactions of starch is the formation of a blue color with iodine. This is supposed by some to be merely a physical combination, but more generally believed now to be a chemical compound. Mylius finds that it contains about eighteen per cent. of iodine, partly as hydrogen iodide, and gives it the formula $(C_{24}H_{40}O_{20}I)_4HI$. Seyfert, accepting the same formula for starch, considers that the iodine compound possesses the formula $(C_{24}H_{40}O_{20})_6I_7$, which requires 18.61 per cent. of iodine. It is not very stable, being decomposed by water on heating. Nevertheless, the blue coloration is constantly availed of to note the presence or gradual disappearance or alteration of starch in many technical processes.

* Bell, The Analysis and Adulteration of Foods, Part ii. p. 86.

The action of dilute acids upon starch brings about the change known as "hydrolysis," and there is produced *dextrine*, $C_{12}H_{20}O_{10}$, and *dextrose*, $C_6H_{12}O_6$, the latter eventually as sole product. Many ferments, like saliva, the pancreatic ferment, and especially the diastase of malt, produce in starch a somewhat similar change, and yield *maltose*, $C_{12}H_{22}O_{11}$, and a number of intermediate products between this and starch. A great deal of investigation has been devoted to these intermediate products, and as yet no absolute agreement has been reached on the subject. The following is the series of products obtained in this hydrolysis of starch as stated by Tollens:*

| | | |
|---|---|---|
| Starch | | gives a blue iodine reaction. |
| Soluble starch (amylodextrine) | | gives a blue iodine reaction. |
| Dextrines | erythrodextrine | gives a violet and red iodine reaction. |
| | achroodextrine | gives no iodine reaction. |
| | maltodextrine | gives no iodine reaction. |
| Maltose | | reduces Fehling's solution, but not Barfoed's reagent. |
| Dextrose | | reduces Fehling's solution, and also Barfoed's reagent. |

Other chemists notably increase the list of these intermediate products. The existence of erythrodextrine as a distinct compound is doubted by some investigators, who consider it to be merely a mixture of achroo- or maltodextrine with a little soluble starch, such a mixture giving a violet reaction with iodine. By over-treatment with acids unfermentable carbohydrates, of a character differing from any of the products named, appear to form. The name *gallisin* has been given to a compound of this kind, and the formula $C_{12}H_{24}O_{10}$ ascribed to it. For a description of the conditions of its formation see later (p. 178).

Strong nitric acid in the cold acts upon starch, producing nitro derivatives, such as mono-, di-, and tetra-nitro-amylose, collectively known as xyloïdin. Alkalies and alkaline earths form combinations with starch, the barium and calcium compounds being insoluble, of which advantage is taken in the Asboth method for determination of starch. (See p. 180.)

## II. Processes of Manufacture.

1. Extraction and Purifying of the Starch.—Of the various starch-containing materials before enumerated, only a limited number are actually utilized for the extraction of the starch in a pure condition,—viz., maize, wheat, rice, potatoes, and arrow-root. In the United States by far the greater amount is obtained from maize, or Indian corn, a limited amount only being extracted from wheat. In Europe, on the Continent, potatoes serve as the chief starch-producing material, some also being extracted from wheat and some from rice, while in the West Indies arrow-root starch is manufactured at St. Vincent and elsewhere.

In the manufacture of corn starch, after winnowing or cleansing the corn by powerful fans, it is placed in large wooden steeping-vats, holding from one thousand to six thousand bushels. It remains here covered with water at a temperature not exceeding 140° F. for from three to ten days, the water being, however, renewed every six hours, and care being taken to prevent any development of fermentation. In the Durgen system, as practised at the Glen Cove Starch Works, a continuous stream of water,

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* Tollens, Kohlenhydrate, Breslau, 1888, p. 177.

heated to 140° F., flows for three days at the rate of ten thousand gallons per day through each tank, after which the corn is sufficiently softened. The softened corn is now ground between burr-stones, a stream of water running continuously into the hopper of the mill. As it is ground, the thin paste is carried by the stream of water upon the shakers, or sieves. These are either revolving sieves or horizontal square shaking sieves. The starch-containing magma is generally reground, and then the paste is passed over the starch-separators. These are inclined sieves of silk bolting-cloth, which are kept in constant motion and are sprayed with jets of water. The starch passes through the bolting-cloth with water as a milky fluid, while the coarser cellular tissue, or husk, of the corn is left behind. This residue is pressed to remove water, and sold as cattle food. The water from the shakers holding the starch in suspension is run into wooden vats, where the starch settles, and the water is drawn off and discarded. The starch is next thoroughly agitated with fresh water, to which a caustic soda solution of 7° to 8° Baumé has been added, until the milky liquid has changed to a greenish-yellow color. The object in adding the alkali is to dissolve and remove the gluten and other albuminoids, oil, etc. After sufficient agitation and treatment with alkali, the separated starch and glutinous matter is allowed to deposit, the supernatant solution of gluten, oil, etc., is allowed to run to waste, and the impure starch washed and agitated with water. It is allowed to stand at rest for fifteen to twenty minutes to permit insoluble gluten to subside, when the top one of a series of plugs arranged in the side of the vat is withdrawn, and the starch suspended in water allowed to flow by means of a gutter into subsiding-vats placed below; then the next lower plug is drawn, and so on until the last plug has been drawn. The plugs are replaced and the vats again filled with water, and the operation repeated as before. This operation, called the siphoning process, is generally repeated three times, and the three runnings of starch are collected in three separate vats, forming the three grades of starch of the factory. These three grades of factory starch are again agitated with water, sieved through bolting-cloth, and run finally as purified starch into wooden "settlers." After it has been compacted sufficiently, which is effected in boxes with perforated bottoms, it is cut into blocks and dried upon an absorbent support of plaster of Paris while heated in a current of warm air. In drying out thoroughly, any remaining impurities come to the surface with the escaping moisture and form a yellowish crust. When this is removed, the interior is found to be perfectly white. The results on a bushel of fifty-six pounds of corn are thus stated by Archbold: *

| | | |
|---|---|---|
| Starch recovered | 28.000 | pounds. |
| Dry refuse for cattle food | 13.700 | " |
| Bran (in cleansing process) | 0.728 | " |
| Moisture of the corn | 5.626 | " |
| Loss (albuminoids, oil, etc.) | 7.946 | " |
| | 56.000 | " |

In the Jebb process for the manufacture of starch from Indian corn, recently introduced, the use of alkali is entirely avoided, and the treatment shortened and simplified by effecting a mechanical separation of both the husk and the germ of the corn before the starchy part of the corn is ground.

* Journ. Soc. Chem. Ind., 1887, p. 82.

The ground husk and germ containing the gluten, albuminoids, and oil are sold for cattle food, while the starch in a high state of purity is separately ground and prepared.

In manufacturing starch from wheat two quite different processes are followed, according as the gluten is to be obtained as a side-product or not. In the process generally known as the "sour," or fermentation, process, the gluten is wasted. In this process the wheat is steeped in tanks until thoroughly softened, then crushed in roller-mills, and placed for fermentation in large oaken cisterns. The temperature is here maintained at about 20° C., and the operation lasts some fourteen days, the mass being well stirred during its continuance. The sugar of the wheat and a part of the starch are converted into glucose, which undergoes alcoholic fermentation, and passes by oxidation into the acetous fermentation also, acetic, propionic, and lactic acids being formed. These rapidly attack and dissolve the gluten, liberating the starch-granules. The impure liquor is drawn off from the starch mass, and the latter is washed, either in hempen sacks while being trodden under foot or in drums with perforated sides. After repeated washings and settlings and renewed sieving through fine hair sieves the starch is sufficiently purified. Wheat starch is also obtained from wheat flour without fermentation by what is known as Martin's process, in which a stiff dough is made of the flour. This is then washed in a fine sieve under a jet of water till all the starch has escaped as a milky fluid. This leaves the gluten, of which about twenty-five per cent. of the weight of the flour is gotten suitable for use in the manufacture of macaroni, or to be used instead of albumen or casein in calico-printing.

In the manufacture of potato starch, the potatoes are washed and then pulped by a grating or rasping machine. The grated mass, made into a paste with water, then goes at once into the sieving machine, where it is rubbed by revolving brushes against the wire or hair sides of the rotating cylinder, while a current of water is continuously washing out the fine starch from the pulp. The sifted and washed starch deposits in large tanks, where it is repeatedly washed by agitation and settling with fresh waters. It is then spread out on absorbent slabs to dry, or is dried in centrifugals or filter-presses.

2. Manufacture of Glucose, or Grape-sugar.—As stated on a preceding page, the action of dilute acids converts starch into dextrine, maltose, and dextrose, the last of which becomes by continued action the sole product. As it is also the most important product of this action of acids, we shall take it up first. The purified starch obtained as described in the preceding section, while yet moist, is taken for the treatment with acids. The "conversion" is accomplished in either open or closed converters, or partly in one and partly in the other. The open converters are wooden vats, generally of three thousand to four thousand gallons capacity, and serve to treat the starch from one thousand bushels of corn. They are provided with copper steam-coils, either closed or perforated. Sulphuric acid is generally employed in the conversion, though other acids have been used. The quantity of the acid employed varies with the object of the manufacturer. For the production of "glucose," a liquid product which contains much dextrine, a smaller quantity is used than when solid "grape-sugar" is to be produced, in which the conversion into dextrose is much more complete. The proportion varies from one-half pound oil of vitriol to one and a quarter pounds per hundred pounds of starch. When the open converter

is used, a few inches of water is introduced and the acid added, or half the acid may be added to the starch mixture. The acid water is brought to a boil, and the starch, previously mixed with water to a gravity of from 18° to 21° Baumé, is slowly pumped in, keeping the liquid constantly boiling. When all the starch has been introduced, the whole is boiled until the iodine test ceases to give a blue color and shows a dark cherry color. The boiling is usually continued for about four hours. The closed converters may be made from strong wooden vats or may be of copper ; they are provided with safety-valves, and are made of sufficient strength to stand a pressure of six atmospheres. Fig. 57 shows the form first introduced in this country by T. A. Hoffmann, while Fig. 58 shows the form proposed by Maubré in London. In this case the starch is mixed with water to a gravity of from 11° to 16° Baumé. This with the acid is introduced into the converter, and the whole is heated under a pressure of from forty-five to seventy-five pounds per square inch. The time required for the conversion is much shorter than in the open converters. The use of open and closed converters successively is often resorted to. The starch and water of a gravity of 15° or 16° Baumé is first boiled in the open converter for from one to two hours, then transferred to the closed converter and boiled under a pressure of from forty-five to seventy-five pounds per square inch. The time of this boiling varies from ten minutes to half an hour.

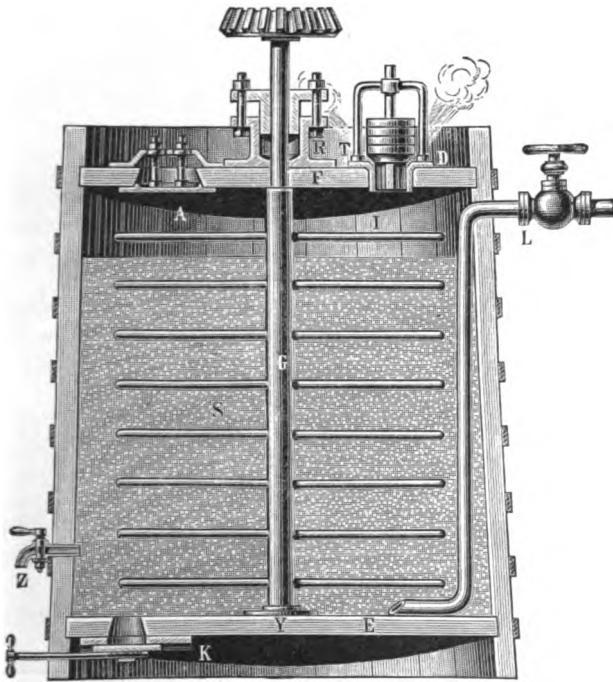
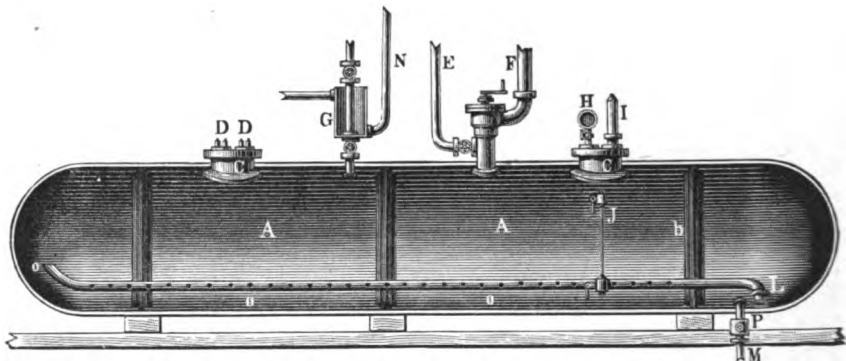



Fig. 57.

When the starch has been sufficiently converted, according to the product desired, the liquor is run into the neutralizing-vats. Here a sufficient quantity of marble-dust is added to completely neutralize the sulphuric acid. A little fine bone-black is generally added at the same time. It is then allowed to cool and deposit the sulphate of lime. The liquor having a gravity of 12° to 18° Baumé, and known as "light liquor," is next filtered through bag filters of cotton cloth or filter-presses. In many establishments the liquor is now treated with sulphurous acid gas to prevent fermentation, and probably to some extent to act as a bleaching agent. It is then filtered through bone-black, by which it is decolorized and at the same time freed from various soluble impurities. Concentration is then effected in the vacuum-pan at

a temperature of about 140° F. until it has a gravity of from 28° to 30° Baumé, when it is called "heavy liquor." A second bag or filter-press filtration is now resorted to in many factories to remove the sulphate of lime, which separates out at this degree of concentration. It is then filtered a second time through bone-black to secure complete decolorization and purification. The final concentration is effected by boiling the liquor in the vacuum-pan until it reaches 40° to 42° Baumé. That product in which the conversion has been least complete remains liquid, and is called "glu-

FIG. 58.

cose" in the trade; that which is ready to solidify is known as "grape-sugar." Dr. Arno Behr has patented a process for obtaining the solid grape-sugar in pure crystals. While it is still liquid there is added to it a small quantity of crystallized anhydrous dextrose. The mixture is filled into moulds, and in about three days it is found to be a solid mass of crystals of anhydrous dextrose. The blocks are then placed in a centrifugal machine to throw out the still liquid syrup, and the anhydrous dextrose remains as a crystalline mass.

3. MANUFACTURE OF MALTOSE.—By the action of the diastase of malt upon starch is formed mainly maltose. Dilute sulphuric acid will convert this by prolonged boiling into dextrose, but diastase alone will not so convert it. The manufacture of maltose on a large scale as a preparation for use in beer-brewing to simplify the preparation of a suitable wort has been attempted by several. Dubrunfaut and Cuisinier patented a process in 1883 for preparing maltose, either as syrup or crystallized, by the following procedure: One part of green or partially dried malt is warmed with two to three parts of water, digested for several hours at 30° C., and afterwards filter-pressed to obtain an "infusion" of malt. One part of starch-flour is then suspended in two to twelve parts of water, and five to ten per cent. of infusion added, the whole gradually warmed to 80° C., then heated under a pressure of one and a half atmospheres for thirty minutes, quickly cooled to 48° C., and treated with five to twenty per cent. of infusion and hydrochloric acid (from six to twenty-five cubic centimetres of acid per one hundred litres). After one hour the mass is filtered through filter-paper fastened upon linen cloth. The solution is allowed to stand at 48° C. for twelve to fifteen hours, then concentrated to 28° B., filtered, again concentrated to 38° B., filtered through animal charcoal, and allowed to crystallize. A sample of the syrup made from corn-starch by the Brussels Maltose Com-

pany working under this patent was analyzed by Märcker,* and found to contain 19.8 per cent. water, 78.7 per cent. maltose, 1.5 per cent. non-sugar, and no dextrine. The process is, however, said to have failed as yet of commercial success. Saare,† who has recently investigated it, shows that the complete conversion into maltose only takes place with weak mashes, and he concludes from his results that the process is not suitable for German distilleries under the present conditions. O'Sullivan and Valentin ‡ have also patented a process for producing from starch, or starch-yielding substances, preferably from rice, a compound solid body, which the inventors term "dextrine-maltose," consisting of the same proportional quantities of dextrine and maltose as are ordinarily obtained from malt by a properly-conducted mashing process, and which it is intended should replace a portion of the malt used in brewing. For details, see original article. Perfectly pure maltose can be obtained by Herzfeld's process of repeatedly extracting with alcohol from the syrupy product of the action of malt upon starch. The alcohol precipitates the dextrine, but dissolves the maltose, which can then be obtained in crystalline condition.

4. MANUFACTURE OF DEXTRINE.—This may be effected by acting upon starch with heat alone, by the action of dilute acids and heat, or by the action of diastase. The first and second of these methods are followed in preparing the solid product. In the manufacture by heat alone the limits of temperature are 212° to 250° C., although Payen says that 200° to 210° C. produces the most perfectly soluble dextrine. The starch is heated in revolving drums, which are frequently double-jacketed, and contain oil in the outer space in order to insure uniform heating. After the moisture is given off, the loss of weight in roasting is small, two hundred and twenty pounds of starch giving one hundred and seventy-six pounds of finished dextrine.

In the manufacture by the aid of acids the starch is mixed with dilute nitric or hydrochloric acid so as to form a damp powder. This is exposed to a temperature of 100° to 120° C. until the transformation is complete, which can be determined by applying the iodine test from time to time. The process must be arrested promptly when the starch is all changed, or the dextrine will pass rapidly into glucose. Oxalic acid is also sometimes employed in the manufacture of dextrine.

5. MANUFACTURE OF SUGAR-COLORING (*Caramel, or Zucker-couleur*).—Very considerable quantities of an artificial coloring material for use in coloring beer, rum, cognac, and high wines is made on the Continent of Europe from starch. For the manufacture of rum and cognac coloring, starch is treated with dilute sulphuric acid, as before described for the manufacture of dextrose and dextrine mixtures, but the heating is continued until all the dextrine has been changed into dextrose, as determined by taking a sample from time to time and testing it with an excess of ninety-six per cent. alcohol. When no longer any turbidity from separated dextrine shows, the reaction is considered as finished. The sulphuric acid is then neutralized with carbonate of lime, and after sufficient standing the clear liquor is run off from the precipitated sulphate of lime. It is now concentrated to 36° B. and filtered. The hot filtrate is then run into a vessel provided with

* Jahresber. der Chem. Tech., 1886, p. 613.
† Dingler, Polytech. Journ., 266., p. 418.
‡ Journ. Soc. Chem. Ind., 1888, p. 446.

mechanical agitation and heated to boiling, when crystallized soda salt (three kilos. of soda to one hundred kilos. of sugar solution) is added in small portions at a time. The contents of the kettle froth and must be continuously stirred. White and inflammable vapors are given off and the color rapidly deepens. The heat is now gradually lessened to prevent carbonizing of the contents of the vessel, and the color is tested. A drop chilled by being dropped into water should harden and be brittle and should taste bitter. The contents of the kettle are then cooled at once by running in hot water. When the production of the color is completed, the contents of the kettle are extracted with water, filtered to remove carbonized particles, and then tested as to quality. The coloring is made in several grades or depths of color, which are also differently soluble, the one in seventy-five per cent. alcohol and the other in eighty per cent. alcohol. For beer- or wine-coloring it is not necessary to be so careful to use a glucose freed perfectly from dextrine, and, instead of soda, ammonium carbonate is taken. The product is soluble in water, but not so readily in alcohol.

## III. Products.

1. STARCH.—The properties and action of reagents upon starch have already been noted in speaking of it as a raw material. It is only necessary to subjoin a few analyses of commercial starches in order to show the character of that usually obtainable. Those of potato and wheat starch are by J. Wolff, as quoted in "Wagner's Chemical Technology," and those of corn starch are by Dr. Archbold, as given by him in the "Journal of the Society of Chemical Industry," 1887, p. 188.

| PERCENTAGE COMPOSITION. | Potato starch. (Wolff.) | Wheat starch, I. (Wolff.) | Wheat starch, II. (Wolff.) | Corn starch, I. (Archbold.) | Corn starch, II. (Archbold.) | Corn starch, III. (Archbold.) |
|---|---|---|---|---|---|---|
| Starch | 83.59 | 83.91 | 79.63 | 98.50 | 92.88 | 90.33 |
| Gluten | ... | 0.10 | 1.84 | ... | } 2.38 | } 4.25 |
| Cellulose | 0.50 | 1.44 | 3.77 | ... | | |
| Ash | 0.53 | 0.03 | 0.55 | 0.30 | 0.60 | 0.65 |
| Water | 15.38 | 14.52 | 14.20 | 1.20 | 4.14 | 4.77 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

2. GLUCOSE AND GRAPE-SUGAR.—Starch-sugar appears in commerce in a great variety of grades and under a similar variety of names. As already said, in the United States the name glucose is in general applied to the liquid products, while that of grape-sugar is given to the solid products. In France, where large quantities of similar products are manufactured, the liquid product is known as "sirop cristal" and the solid product "glucose massé." The following analyses show the composition of the commercial products, the first five being American products as examined by the Committee of the National Academy of Sciences,* and the last two being French as examined by L. von Wagner: †

* Report on Glucose, Washington, 1884, p. 22.
† Dingler, Polytech. Journ., 266, p. 470.

| Percentage Composition. | I. Glucose solution. | II. Glucose solution. | III. Glucose solution. | Solid grape-sugar. | Crystallized grape-sugar. | "Sirop cristal." | "Glucose massé." |
|---|---|---|---|---|---|---|---|
| Dextrose . . . . . | 36.5 | 36.5 | 39.0 | 72.1 | 99.4 | 64.0 | 64–66 |
| Maltose . . . . . | 19.3 | 7.6 | . . . | . . . | . . . | . . . | . . . |
| Dextrine . . . . . | 29.8 | 40.9 | 41.4 | 9.1 | . . . | 21.0 | 18–22 |
| Water . . . . . . | 14.2 | 15.3 | 19.3 | 16.6 | 0.6 | 15.0 | 15–18 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

3. Maltose.—Maltose forms fine white crystalline needles aggregating in warty groups, which have a faint sweetish taste. It is soluble in water and methyl and ethyl alcohol, but more difficultly in the last than dextrose. Its formula is $C_{12}H_{22}O_{11}$, and it crystallizes with one molecule of water, which it loses slowly at 100° C. in a vacuum. Its specific rotatory power is, according to Meissl, $(S)_D = 140.375 - .01837\ P - .095\ T$, where $P$ equals the percentage strength of the solution and $T$ the temperature. A ten per cent. solution at 20° C. would then be 138.3°. O'Sullivan takes it as 139.2° for a ten per cent. solution. Its reducing power with Fehling's solution is frequently stated to be two-thirds that of dextrose, but Brown and Heron as well as O'Sullivan make it more exactly sixty-two per cent. of that shown by dextrose. It has no action, however, upon Barfoed's reagent (see p. 180), which is reduced by dextrose. Maltose is said to be directly and completely fermentable without previous change into dextrose, but more slowly than this latter, so that if a mixture of maltose and dextrose be fermented with yeast, the whole of the dextrose disappears before the former sugar is acted upon.

4. Dextrine.—Pure dextrine is a white amorphous solid. It is tasteless, odorless, and non-volatile. It is completely soluble in cold water, but the commercial varieties usually leave from twelve to twenty per cent. or even more of starch and other insoluble residue when dissolved. Heated with dilute acids it yields maltose and ultimately dextrose. It is unfermentable if free from sugar. It has no reducing power on Fehling's solution. Probably what is called dextrine is a mixture of products obtained in the breaking down of the complex starch-molecules. Some investigators claim to have obtained sixteen distinct modifications or varieties of dextrine in this way. We have before (see p. 170) alluded to amylodextrine, erythrodextrine, achroodextrine, and maltodextrine.

Commercial dextrine, or "British gum," gives a brown coloration with iodine, and probably consists largely of erythrodextrine. The following analyses by R. Forster give an idea of the composition of the dextrines usually obtainable:

| Percentage Composition. | First quality dextrose. | Dark-burned starch. | Brown dextrine. | Gommeline. | Old dextrine. | Light-burned starch. |
|---|---|---|---|---|---|---|
| Dextrine . . . . . . . | 72.45 | 70.43 | 63.60 | 59.71 | 49.78 | 5.34 |
| Sugar . . . . . . . . | 8.77 | 1 92 | 7.67 | 5 76 | 1.42 | 0.24 |
| Insoluble . . . . . . . | 13.14 | 19.97 | 14.51 | 20.64 | 30 80 | 86.47 |
| Water . . . . . . . . | 5.64 | 7.68 | 14.22 | 13.89 | 18.00 | 7.95 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

Dextrine is used as a substitute for natural gums, especially for gum arabic. It is thus used in calico-printing and in the mordanting and printing of colors upon most other classes of textile goods, for mucilage, for glazing cards and paper, as warp-dressing, and in the manufacture of beer. It forms the crust on bread by the change of the starch of the flour in baking, and is present in most products from starch or starch-sugar.

5. UNFERMENTABLE CARBOHYDRATES (*Gallisin*).—The presence of an unfermentable carbohydrate in starch-sugar was long since pointed out by O'Sullivan. The compound which has been specially studied is known as gallisin, and is prepared by fermenting a twenty per cent. solution of starch-sugar with yeast at 18° or 20° C. for five or six days. The resultant liquid was filtered, evaporated to a syrup at 100° C., and shaken with a large excess of absolute alcohol. The treatment with alcohol was repeated several times until the unaltered sugar and other impurities were removed, the syrup being converted into a yellowish crumbling mess, which, by pounding in a mortar with a mixture of equal parts of alcohol and ether, was obtained as a gray powder. After purifying with animal charcoal and drying over sulphuric acid, the gallisin was obtained as a white amorphous extremely hygroscopic powder. Its taste is at first sweet, but afterwards becomes insipid. It is easily decomposable by heat, even at 100° C. It is readily soluble in water, nearly insoluble in absolute alcohol, and but slightly more soluble in methyl alcohol, in which respect it differs from dextrose. Gallisin is stated to have the composition $C_{12}H_{24}O_{10}$. Its concentrated aqueous solution is distinctly acid to litmus and a sparingly soluble barium compound may be obtained therefrom by adding alcoholic baryta. It reduces nitrate of silver on heating, especially on addition of ammonia, reduces bichromate and permanganate, and precipitates hot Fehling's solution. Its cupric oxide reducing power (dextrose = 100) is stated to be 45.6°. Gallisin is dextro-rotatory, the value for $S_D$ being stated to be 80.1° in twenty-seven per cent., 82.3° in ten per cent., and 84.9° in 1.6 per cent. solutions. By heating with dilute sulphuric acid for some hours gallisin yields a large proportion of dextrose, but its complete conversion has not so far been effected.

It is doubtful whether "gallisin" as hitherto obtained is really a definite compound, but the possibility of isolating a reducing or optically active body from the liquid left after fermenting solutions of many specimens of starch-sugar cannot be ignored in considering the composition of commercial glucose.

## IV. Analytical Tests and Methods.

1. FOR STARCH.—The usual method for the determination of starch is to invert by the action of dilute acid, and then determine the dextrose produced by the aid of Fehling's solution. In this case one hundred parts of dextrose are taken as indicating ninety of starch. It has been found, however, that the change to dextrose by the aid of dilute sulphuric acid is not complete, that other non-reducing bodies are formed, and that but ninety-five per cent. of the starch is converted into dextrose. The hydrolysis is more completely effected by the aid of hydrochloric acid, as carried out in Sachsse's method. 2.5 to 3 grammes of dry starch (or so much of the starch-containing substance as would correspond to this amount of starch) are placed in a flask with two hundred cubic centimetres of water and twenty cubic centimetres of hydrochloric acid and heated on the water-

bath with inverted condenser for three hours. (Märcker states that heating for three hours with this amount of hydrochloric acid does not give more than ninety-six to ninety-seven per cent. of the starch as sugar, as some of the latter is destroyed. He recommends using fifteen cubic centimetres of acid and heating for two hours.) The contents of the flask are then neutralized with potassium hydrate or sodium carbonate, filled to the mark, and the dextrose determined by Fehling's solution. If other carbohydrates or cellulose are present, which would be also converted into dextrose by hydrochloric acid, the starch must be previously brought into the soluble form, which may be done by heating with water to 130° C. in a pressure-flask like that of Lintner, shown in Fig. 59. Or the starch may be hydrolyzed in part by infusion of malt or diastase at 62.5° C., filtered from cellulose, etc., and then treated with hydrochloric acid for complete hydrolysis as above. In this latter case, the process of Reinke * is the simplest. Three grammes of the sample as finely powdered as possible are heated to boiling with fifty cubic centimetres of water, cooled to 62.5° C., and hydrolyzed for an hour at this temperature with .05 gramme of diastase. This is prepared according to Lintner's procedure, by making an alcoholic twenty per cent. extract (1 : 3) of raw malt, adding to the filtrate two volumes of ninety-six per cent. alcohol, separation of the precipitated diastase, washing with alcohol and ether, and drying in a desiccator. The mixture is then cooled, diluted with water to two hundred and fifty cubic centimetres, and filtered. Of the filtrate, two hundred cubic centimetres are taken and hydrolyzed, as before described, with fifteen cubic centimetres of hydrochloric acid of 1.125 specific gravity for two and a half hours, when the solution is neutralized and the dextrose determined.

FIG. 59.

A more elaborate course of treatment, following in the main the same lines as the procedure of Reinke just described, but stopping with the action of the diastase, has been published by O'Sullivan, and is given at length by Allen.† In this case the filtered liquid, assumed to contain nothing but maltose and dextrine, is made up to one hundred cubic centimetres, and the density determined. It is then tested with Fehling's solution for the maltose, and the dextrine deduced from the rotatory power of the solution. The maltose found, divided by 1.055, gives the corresponding weight of starch, which, added to the dextrine found, gives the total number of grammes of starch represented by one hundred cubic centimetres of the solution.

The method for the determination of starch in cereals most generally used in Germany at present is that of Märcker.‡ Three grammes of sub-

* Jahresber. Chem. Technol., 1887, p. 863.
† Commercial Organic Analysis, 3d ed., vol. i. p. 415.
‡ Jahresber. Chem. Technol., 1885, p. 863.

stance are placed in a small beaker (preferably of metal), which is placed as one of several in a Soxhlet pressure-boiler, or the test is carried out in the Lintner pressure-flask, figured on the preceding page, and heated to the temperature of boiling water. It is then cooled to 60° to 65° C., five cubic centimetres of thin malt infusion are added, and it is digested at this temperature for some twenty minutes. It is then made faintly acid (one cubic centimetre of tartaric acid suffices) and heated under a pressure of three to four atmospheres. It is then cooled down and an additional five cubic centimetres of malt infusion added, with which it is digested an half-hour. The solution is then brought up to one hundred cubic centimetres, filtered, and determined with Fehling's solution, either by titration or by weighing the reduced copper.

Of other methods proposed for starch determinations it is only necessary to notice the Asboth method, proposed in 1887. It depends on the fact that starch forms a compound with baryta-water, $C_{24}H_{40}O_{20}BaO$, containing 19.1 per cent. of BaO, which is insoluble in forty-five per cent. alcohol. The baryta-water is used in excess, and the free alkaline earth determined by titration with decinormal hydrochloric acid. Numerous experimenters have taken exception to the method that the results were variable, and that starch combined with varying amounts of barium oxide. To these objections the author has recently replied,* and claims that the presence of fat in the cereals interferes with the accuracy of the determination, and that if the fat be previously extracted by ether, the determinations in the fat-free residue are accurate and concordant. J. Napier Spence, in the "Journal of the Society of Chemical Industry" for 1888, p. 77, has also come to the defence of the Asboth method and shown the conditions under which it yields accurate results.

2. Glucose, or Dextrose.—For the determination of dextrose alone the Fehling's solution affords the most accurate means. For its use, see analysis of raw sugars, p. 158. In the absence of any other optically active body its examination with the polariscope will also suffice. For mixtures like commercial glucose, which contains dextrose, maltrose, and dextrine, see later.

3. Maltose.—This variety of sugar, as before stated, has optical activity and reducing power on Fehling's solution. It can, however, be distinguished from dextrose by its failure to reduce Barfoed's solution, which is reduced by dextrose and invert sugar. This reagent is made by dissolving one part of neutral copper acetate in fifteen parts of water, to two hundred cubic centimetres of which five cubic centimetres of thirty-eight per cent. acetic acid is added. Boiled for several minutes with maltose solution it shows no reduction.

4. Dextrine.—Pure dextrine differs from dextrose and maltose in showing no reducing power with either Fehling's solution or with Knapp's mercuric cyanide solution. It can, indeed, be freed from admixture with dextrose and maltose by heating with an excess of an alkaline solution of mercuric cyanide, which oxidizes these two varieties of sugar, leaving the dextrine unaffected. (See Wiley's method on next page.)

5. Commercial Glucose and Similar Mixtures derived from Starch.—As commercial glucose is likely to be a mixture of the three compounds, dextrose, maltose, and dextrine, its analysis and the determination of the several constituents becomes a frequently-recurring problem.

* Chemiker Zeitung, 1889, pp. 591 and 611.

Three methods have been proposed. The first, by Allen,* requires the determination of moisture and ash in the sample, which, subtracted from 100, leaves the total organic solids, $O$. The apparent specific rotatory power, $S$, and the cupric oxide reducing power (in terms of dextrose reduction = 100), $K$, are now determined. Then, if $m$ be the maltose, $g$ the dextro-glucose, and $d$ the dextrine, Allen determines the respective percentages by the use of the formulas $m = \left(S - \frac{52.7\,K + 198\,(O - K)}{100}\right) \div .313$, $g = K - .62\,m$, and $d = O - (g + m)$. The author states that the presence of gallisin or other unfermentable sugar may vitiate the values of $K$ and $S$, as observed, and so make the results inaccurate.

The second method is that of Wiley,† which is based upon the theory that boiling with an alkaline solution of mercuric cyanide will destroy the optical activity of maltose and dextrose, leaving that of dextrine unchanged. The cupric oxide reducing power of the sample is ascertained in the usual way by Fehling's solution. The specific rotatory power is determined by polarizing a ten per cent. solution (previously heated to boiling) in the ordinary manner. Ten cubic centimetres of this solution used for polarizing are then treated with an excess of an alkaline solution of mercuric cyanide, and the mixture boiled for two to three minutes. It is then cooled and slightly acidulated with hydrochloric acid, which destroys the reddish-brown color possessed by the alkaline liquid. The solution is then diluted to fifty cubic centimetres, and the rotation observed in a tube four decimetres in length. The angular rotation observed will be due simply to the dextrine, the percentage of which may then be calculated by the formula $\frac{\text{rotation} \times 1000 \times \text{cubic centimetres of solution polarized}}{198 \times \text{length of tube in centimetres} \times \text{weight of the sample taken}} =$ percentage of dextrine. The percentages of dextrose and maltose may be deduced from the reducing power of the sample, or from the difference in specific rotatory power before ($S$) and after ($s$) the treatment with alkaline mercuric cyanide. Thus, $K = 1.00\,g + .62\,m$, $S = .527\,g + 139.2\,m + 1.98\,d$ and $s = 1.98\,d$, whence $m = \frac{S - s - .527\,K}{1.06526}$. $g$ can now be found from the first of the three equations, and then $d$ in the second. Wiley's process was employed by the Committee of the National Academy of Science in their investigation of commercial glucose from corn starch. It is, however, based upon several assumptions that have not been specifically proven, and especially in the presence of any considerable quantity of maltose are its results open to doubt. (See Allen, "Commercial Organic Analysis," 3d ed., vol. i. p. 369, foot-note.)

The third method of estimating the constituents in commercial glucose is due to C. Graham, and is probably more exact than either of those before mentioned. Dissolve five grammes of the sample in a small quantity of hot water and add the solution drop by drop to one litre of nearly absolute alcohol. Dextrine is precipitated, and on standing becomes attached to the sides of the beaker, while maltose, gallisin, and dextrose are soluble in the large quantity of alcohol employed. If the solution be then decanted from the precipitate, the dextrine in the latter can be ascertained by drying and weighing, or by dissolving it in a definite quantity of water and observing the

* Commercial Organic Analysis, 3d ed., vol. i. p. 365. † Chemical News, xlvi. p. 175.

solution, density, and rotation. The alcohol is distilled off from the solution of the sugars and the residual liquid divided into aliquot portions, in one of which the gallisin may be determined after fermentation with yeast, while others are employed for the observation of the specific rotation and reducing power, which data give the means of calculating the proportions of maltose and dextrose in the sample.

## V. Bibliography and Statistics.

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### STATISTICS.

1. PRODUCTION OF STARCH IN THE UNITED STATES AND GERMANY.—O. Saare in 1896 gave the following summary of the production in these chief producing countries:

| | United States. Hundred kilos. | Germany. Hundred kilos. |
|---|---|---|
| Potato starch | 120,000 – 180,000 | 2,000,000 – 3,000,000 |
| Corn starch | 2,000,000 – 3,000,000 | 25,000 – 50,000 |
| Wheat starch | 150,000 – 200,000 | 50,000 – 100,000 |
| Rice starch | ... ... | 200,000 – 250,000 |
| | 2,270,000 – 3,380,000 | 2,275,000 – 3,400,000 |

2. PRODUCTION OF GRAPE-SUGAR (STARCH-SUGAR), GLUCOSE, DEXTRINE, ETC.—The same authority gives the following figures for the products from starch:

| | United States. Hundred kilos. | Germany. Hundred kilos. |
|---|---|---|
| Grape-sugar and glucose syrup | 2,500,000 – 3,000,000 | 350,000 – 400,000 |
| Sugar-color (caramel) | ... ... | 30,000 – 40,000 |
| Dextrine | 20,000 – 50,000 | 150,000 – 180,000 |
| | 2,520,000 – 3,050,000 | 530,000 – 620,000 |

3. PRODUCTION OF STARCH-SUGAR IN FRANCE.—

| | | | |
|---|---|---|---|
| 1887–88 | 34,124,079 kilos. | 1890–91 | 41,494,243 kilos. |
| 1888–89 | 33,439,989 " | 1891–92 | 38,223,645 " |
| 1889–90 | 39,816,476 " | 1892–93 | 38,641,347 " |

4. EXPORTATIONS OF STARCH AND GLUCOSE FROM THE UNITED STATES.—

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| Starch (pounds) | 81,829,435 | 79,088,876 | 72,806,313 | 110,193,776 |
| Valued at | $885,198 | $1,665,926 | $1,371,549 | $2,292,843 |
| Glucose (pounds) | 171,231,650 | 194,419,250 | 196,864,605 | 229,003,571 |
| Valued at | $2,772,335 | $2,736,674 | $2,871,839 | $3,624,890 |

# CHAPTER VI.

## FERMENTATION INDUSTRIES.

### *A.* NATURE AND VARIETIES OF FERMENTATION.

THE word fermentation in the broader sense is applied to those changes whereby in the presence of a body called a ferment many organic bodies, notably the carbohydrates, are decomposed into simpler compounds, although not necessarily into the ultimate products of decomposition.

The ferments which seem to determine the decomposition may be either soluble unorganized ferments, or insoluble organized ferments, which are, in fact, minute vegetable growths. With the soluble ferments, such as diastase, invertin (or sucrase), emulsine, or myrosine, pepsine, trypsine, and papäine, which act upon carbohydrates, glucosides, and albuminoids, we are not now concerned, although the first and second of those mentioned play a very important part in the hydrolysis of starch and cane-sugar.

The organized ferments or vegetable growths may be divided into three classes: first, mould-growths; second, yeast-plants, or the different species and varieties of *Saccharomyces;* and, third, bacteria, belonging to the two genera *Schizomycetes* and *Schizophycetes.* The most important fermentations from an industrial point of view are the alcoholic, which is brought about mainly * by the presence of ferments of the second class, and the acetic and lactic, which are brought about by ferments of the third class. Upon the alcoholic fermentation depend three important groups of industries,—viz., the manufacture of malt liquors, the manufacture of wines, and the manufacture of ardent spirits, or distilled liquors. Upon the acetic fermentation depends the manufacture of different varieties of vinegar, and upon the lactic fermentation the manufacture of cheese and other milk products.

The alcoholic fermentation is always meant when we use the word fermentation in the narrower sense, as with reference to the change which starch and saccharine bodies most generally undergo. In this fermentation, the action of the yeast-plant seems to differ according to the variety of sugar presented to it. Dextrose is most immediately acted upon, the main reaction being $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, although, as Pasteur first showed, side-products like glycerine and succinic acid are also formed, and in practice only about ninety-five per cent. of the dextrose is decomposed by the main reaction. Cane-sugar is not immediately fermentable. If it has been previously exposed to the action of dilute acids, it is changed into invert sugar, which then acts like dextrose. The yeast-plant can effect the same change itself. Invertin (or invertase, as it is also termed) is a soluble ferment existent in yeast. It has the property of rapidly and completely effecting the transformation of cane-sugar into invert sugar, but is without

* Buchner (1897) has shown clearly that there is present in the yeast-cells, even when dead, a soluble ferment or enzyme capable of developing the alcoholic fermentation.

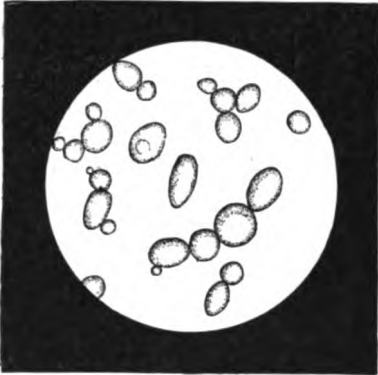
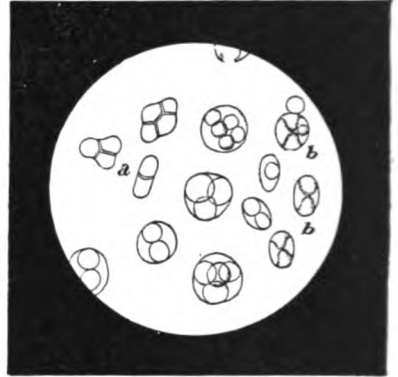
sensible action on dextrose, levulose, maltose, or milk-sugar. Towards dextrine its action is not so certainly negative.

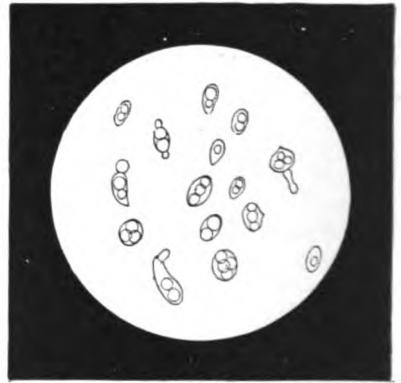
The conditions of the activity of the yeast-plant have been studied by many chemists, but notably by Pasteur. It has been found that if an abundance of air is supplied the plant grows and multiplies but fermentation proceeds very slowly, when the supply of air is limited, the fermentation proceeds more rapidly while the growth of the cells is largely arrested, and that in the absence of air the fermentation proceeds with greatest rapidity, although the plant-cells do not grow any longer, but gradually disintegrate and die. Pasteur's dictum, that "fermentation is the consequence of life without air," is no longer taken as strictly accurate, as with the cessation of the growth and extension of the yeast-plant (which is dependent upon air like the life of any other plant), although its fermentative activity then becomes greatest, it begins at the same time a decay which leaves it after a time dead and inactive.

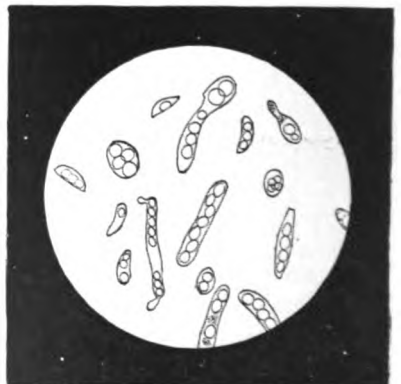
The genus *Saccharomyces* has already been alluded to as the active agent in the alcoholic fermentation. The species *Saccharomyces cerevisiæ* is generally known as the special beer ferment and the *Saccharomyces ellipsoideus* as the wine ferment. Moreover, of the *Saccharomyces cerevisiæ*, two well-marked varieties have been recognized. The one is the most active at the ordinary temperature (16° to 20° C.), and carries through its fermentative work in from three to four days; the other works at a lower temperature (6° to 8° C.) and the fermentation is much slower. The first, placed in a saccharine liquid, is carried by the carbon dioxide which it liberates to the surface of the liquid, where it continues its activity; it is therefore known as a surface or top yeast. The second, on the contrary, is not carried up, and rests during its entire activity on the bottom of the fermenting vessel, and is hence called a bottom yeast. Two quite distinct methods of beer-brewing are practised (see p. 191), depending upon the use of the one or the other of these varieties of yeast. It has been found, however, in practice that, even when a top yeast is used exclusively or a bottom yeast exclusively, the results are not always uniform. These anomalies are now made clear through the researches of E. Ch. Hansen, of Copenhagen, who has applied the methods of pure cultivation introduced by bacteriologists to the study of the yeast-plant. He has found that if a single yeast-cell of one of the better varieties of *Saccharomyces* be cultivated with the precautions needed to exclude what is called "wild yeast" (germs present in the air, notably in the summer months), absolutely uniform results can be gotten in brewing. Beginning in 1883, he has developed the study, and it has now been accepted by most of the leading authorities on fermentation. He first described six species: *Saccharomyces cerevisiæ* I., *Saccharomyces Pastorianus* I., II., and III., *Saccharomyces ellipsoideus* I. and II., of which the second, fourth, and sixth cause bitterness and turbidity (so-called "diseases" in beer). He has since * increased the list of varieties of ferments studied to forty, including both top and bottom yeasts, ferments similar to yeast but not belonging to the genus *Saccharomyces*, and forms of mould-growth. He divides the representatives of each genus into two groups according as they secrete invertin or not.

Fresh yeast resembles a dirty yellowish-gray sediment of unpleasant odor and acid reaction, made up of an immense number of vegetable cells.

* Journ. Soc. Chem. Ind., 1889, p. 471.

**Fig. 60.**

Saccharomyces cerevisiæ.
(After Hansen.)

Saccharomyces cerevisiæ. Ascospores.
(After Hansen.)

**Saccharomyces ellipsoideus.
(After Hansen.)**

**Saccharomyces ellipsoideus. Ascospores.
(After Hansen.)**

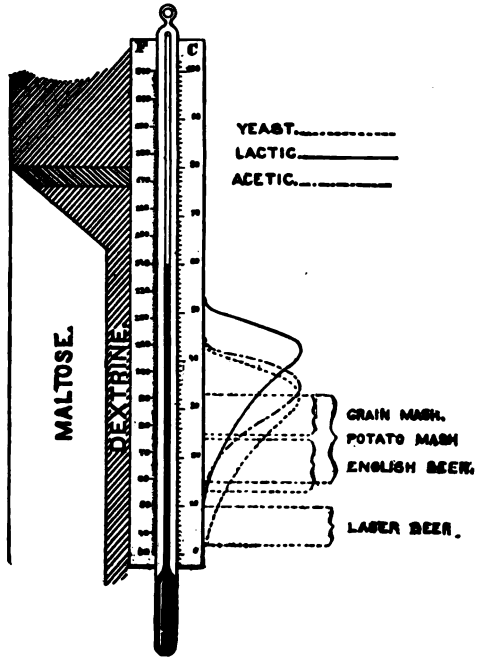
**Saccharomyces Pastorianus.
(After Hansen.)**

**Saccharomyces Pastorianus. Ascospores.
(After Hansen.)**

Three of the pure culture varieties of yeast-plant as obtained by Hansen are shown in the illustration, Fig. 60, together with the special appearance of the ascospores of the same. Of these, the *Saccharomyces cerevisiæ* and *Saccharomyces Pastorianus* are beer ferments, while the *Saccharomyces ellipsoideus* is the wine ferment. For many purposes (bread-baking, use in distilleries, etc.) it is prepared as compressed yeast in cakes, generally with the addition of potato starch.

The special conditions of the alcoholic fermentation are: first, an aqueous solution of sugar of the strength of one part sugar to four to ten parts water; second, the presence of a yeast ferment. If this is not added already developed and active, or if the fermentation is to be spontaneous,—that is, brought about by spores from the air,—the conditions for the development of these spores must also be present. There must be protëin compounds and phosphates of the alkalies and alkali earths. Thirdly, the temperature must remain within the limits 5° to 30° C., or, more generally, from 9° to 25° C. Above 30° C. the alcoholic fermentation readily passes into the butyric and other decomposition.

Fig. 61.



The effect of temperature upon the several different ferments is shown in the graphic illustration of Fig. 61, which represents also the influence of temperature upon the decomposition of starch by diastase. On the right side of the figure, the regularly-dotted line represents the yeast curve. A slight fermentation is already induced at a temperature very little over the melting point of ice. As the temperature rises its activity increases until the maximum is reached, at about 33° C. (92° F.), when it diminishes down to nothing again, and at 50° C. (122° F.) or thereabouts it is killed. The activity of the acetic ferment is repeated at the same time by the irregularly-dotted line, and that of the lactic ferment by the uniform black line.

## *B.* MALT LIQUORS AND THE INDUSTRIES CONNECTED THEREWITH.

### I. Raw Materials.

1. Malt.—Malt is prepared by steeping barley or other grain in water, and allowing it to germinate in order to change the character of the albuminoids and develop the ferment diastase, which then begins to act upon the starch, the germination and change being stopped at a certain stage by heating in a kiln. The composition of the unmalted barley was given among other

cereals on p. 169. The changes which it undergoes in composition by the process of malting will be seen by comparing this with the two analyses of pale malt following, which are by O'Sullivan:

| | No. I. | No. II. |
|---|---|---|
| Starch | 44.15 | 45.13 |
| Other carbohydrates (of which sixty to seventy per cent. consist of fermentable sugar), inulin and similar bodies soluble in cold water | 21.23 | 19.39 |
| Cellular matter | 11.57 | 10.09 |
| Fat | 1.65 | 1.96 |
| Albuminoids soluble in water | 6.71 | 5.31 |
| Albuminoids insoluble in water | 6.38 | 8.49 |
| Ash | 2.60 | 1.92 |
| Water | 5.83 | 7.47 |
| | 100.00 | 100.00 |

O'Sullivan states that malt contains no ready-formed dextrine, but that it does contain from sixteen to twenty per cent. of fermentable sugars, of which about one-half is probably maltose, and due to the transformation of starch in the malting process, while the remainder exists ready formed in the barley, and is not identical with the sugar produced in the malting.

Besides the diastase, a second soluble ferment is formed during the malting process, the so-called peptase, which in the mash process changes the proteids of the malt into peptones and parapeptones, which give nutritive value to the beer.

A high percentage of starch in the barley to be used for brewing is desirable in order that when malted it may yield a large amount of "extractive matter." According to Lintner and Aubry,* a good malt should yield at least seventy-one per cent. of extract reckoned on the weight of dry substance. This determination of the value of a sample of malt is one of the most necessary of analytical tests for the malster or brewer. (See p. 197.)

Well-malted barley is always yellow or amber-colored, shading to brown. On breaking the grain, the interior should be of a pure white color and floury appearance, except when the drying has been intentionally carried so far as to partially caramelize the sugar.

Malted wheat, corn, and rice are at times used as partial substitutes for the barley malt, as well as potato starch and starch-sugar. The use of patented maltose and maltose-dextrine preparations has already been referred to. (See p. 175.)

2. HOPS.—Hops are the female unfructified blossoms (catkins) of the hop-plant (*Humulus lupulus*). Under the thin membranous scales of the strobile or catkin is an abundance of a yellowish resinous powder, consisting of minute sessile grains, to which the name *lupulin* has been given. The active principles of the hops, contained mainly, but not exclusively, in the lupulin, are: First, the ethereal oil, which is present to the amount of .3 per cent. in the air-dried hops. This is yellowish, of strong odor and of burning taste. It consists of a hydrocarbon, $C_5H_8$, and an oxygenized oil, $C_{10}H_{18}O_2$, which by atmospheric oxidation becomes valerianic acid, $C_5H_{10}O_2$, to which old hops owe their odor. Second, the lupulin also contains a resinous bitter principle, which is easily soluble in alcohol, but difficultly soluble in water, and extremely bitter. This is supposed to be an oxidation product of lupulinic acid, which can be gotten in white crystals, speedily becoming resinous. Both the acid and its oxidation products seem to be

* Jahresber. Chem. Tech., 1882, pp. 840 and 851.

held dissolved in the ethereal oil. Hops also contain tannic acid of a variety allied to moritannic acid and turning iron salts green. Analyses of two well-known Bohemian varieties of hops are given.*

| PERCENTAGE COMPOSITION. | Water. | Ethereal oil. | Soluble in alcohol. | Of which is resin. | Residue from alcohol soluble in water. | | Tannic acid in aqueous extracts. | Ash free from $CO_2$. | Carbon dioxide in 100 of ash. | Sand. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Organic. | Ash. | | | | |
| From Saatz | 9.90 | 0.13 | 20.12 | 14.57 | 11.24 | 5.42 | 2.52 | 10.01 | 8.71 | 0.91 |
| From Auscha | 10.61 | 0.17 | 20.97 | 15.14 | 10.51 | 5.10 | 3.18 | 7.87 | 9.51 | 0.81 |

The blossoms are produced in August, and the strobiles are fit for gathering from the beginning of September to the middle of October, according to the weather. The prompt drying of the fresh-picked hops is necessary in order that they may be safely baled. This drying takes place by the aid of hot air in a so-called hop-kiln at a temperature of about 40° C., the hops being repeatedly turned with a light wooden shovel as they lie spread out upon a false or perforated floor. When dry they are pressed by hydraulic presses into compact bales. Hops are also often treated with sulphurous acid gas from burning sulphur to preserve them, although this sulphuring is oftener used with old hops for the purpose of brightening them in color and improving their appearance.

A number of bitter principles have been mentioned as used at times as substitutes for hops in beer-brewing, although it is doubtful if such substitution is much practised. Among these substitutes have been noted quassia, gentian, picrotoxin, the bitter principle of *Cocculus Indicus*, colchicum, wormwood, and picric acid.

3. WATER.—The water used in malting and brewing must be adapted for the purpose in order to get good results. A pure and soft water or a moderately hard calcareous water will do, but it is indispensable that the water be perfectly free from organic impurities. Continental brewers use soft waters most generally in brewing beers, while English brewers prefer gypsum waters for their ales which are specially designed to keep. This is shown in the character of the water of Burton-on-Trent, which contains notable quantities of calcium and magnesium sulphates, calcium carbonate, and sodium chloride.

## II. Processes of Manufacture.

1. MALTING OF THE GRAIN.—Although malt has been described as a raw material of the brewing industry, the preparation of it from the raw grain is a process so closely connected with the success of brewing that it must be described, and especially, too, because it is often combined under the same direction as the brewing process. The process of changing barley into malt is to be divided into four stages: the steeping, the couching, the flooring, and the kiln-drying. The first three of these stages have to do with the germination or development of the acrospire, or plumule, which as it develops brings about great changes in the chemical constitution of the grain, developing from the albuminoid matter the diastase, which in turn begins to

* König, Nahrungs- und Genussmittel, vol. ii. p. 409.

act upon the starch, forming from it maltose and dextrine. At the same time during the germination atmospheric oxidation is going on at the expense of the starch of the grain, water and carbon dioxide being steadily given off. When the development of the diastase is supposed to have reached the right point, which can only be judged of by the growth of the acrospire, or germ, the fourth stage of the process is reached, and the germ must be killed by heat, which is done in the kiln-drying.

The first process of steeping is to give the grain sufficient moisture to allow germination to begin. For that purpose it is put into wooden, iron, or cemented vats. These are half filled with water and the grain added with constant stirring. The sound grains sink shortly under the water, and the dead or imperfect grains float and can be removed. The water soon takes color and odor, and must be replaced by fresh water. The duration of the steeping is usually forty-eight to seventy-two hours, depending upon the temperature, and in winter-time or with older barley may last considerably longer. The end of the treatment may be told by noting the character of the grain. It has swollen and become nearly sufficiently soft to allow of being pierced with a needle and yet exuding no juice. It has gained from forty to fifty per cent. in weight and increased from twenty to twenty-four per cent. in bulk. To offset this gain due to water absorption, it has lost from one to two per cent. of its substance, partly carried off in the steep water and partly given off as gas. The water is then run off, and after draining it is turned upon the couching-floor, where it remains at first in heaps of from fifteen to twenty-four inches in depth. Here it soon begins to heat up, and a rise in temperature of from 7° to 10° takes place. It also begins to "sweat," and gives off an abundance of carbon dioxide, and an agreeable cucumber-like odor is recognizable. The germination is now under way and the rootlets shoot out. The "couching" stage lasts from twenty-four to thirty-six hours, and during that time the grain must be turned several times. The heated barley must now be spread on the floor in shallow layers so as to check somewhat the rate of growth of the germ, and must be turned from four to six times a day as the growth proceeds. The depth of the layer is at the same time reduced from fifteen to four or five inches. During this time the germinating grain must have an abundance of air. The process lasts from seven to ten or even twelve days, according to the season of the year, and its termination is decided by the length of the germ, which must be about two-thirds that of the grain. The loss in weight during the germinating process, according to Lintner, is ten per cent. of the weight of the grain. The loss comes mainly upon the starch, which has in part been changed into maltose and dextrine, but has mostly been oxidized to water and to carbon dioxide. To more efficiently remove the carbon dioxide which would interfere with the germinating process and to prevent too strong a heating, the pneumatic process of malting has been proposed by Galland. In this process the steeped barley is placed on a perforated floor in thick layers, and a regulated current of moist, well-cooled air is kept passing through it. This process is now replacing the other quite largely. Still another form of mechanical malting apparatus is that of Saladin.* The germination must now be stopped promptly, lest it go too far at the expense of the starch of the grain, and this is best effected by heat. The germinating grain may, however, be simply dried thoroughly in the air and the rootlets

* Dammer's Handbuch der Chemischen Technologie, vol. iii. p. 632.

removed by mechanical means. This constitutes air-dried malt, which is used for some purposes. Most generally it is dried in a kiln at a considerably higher temperature. This must be gradually applied, as if, while the raw malt were full of moisture, it were to be heated strongly, the starch would be gelatinized and the grain made tough, hard, and glassy. It is therefore heated first to about 90° F., and this is gradually raised to 150° F., or even in some cases to 180° F. A light gradual heat produces a "pale" malt, a stronger heat "yellow" or "pale amber," and then "amber" and "brown" malt. The kiln may have two floors, on the upper and cooler of which the moist malt loses its water and then passes on to the lower and hotter floor, where it is heated to the higher limit requisite for developing its empyreumatic odor and flavor, or the heating may all be effected on a single floor, in which case more time is needed for the several stages of heating. Black malt used for coloring is heated in revolving coffee-roasters, and most of the sugar is caramelized.

2. PREPARATION OF THE WORT.—The malt after being cleansed and crushed (not ground fine) is ready for use in what is known as the mashing process. This is designed not merely to extract the maltose and dextrine of the malt, but mainly to allow the diastase of the malt to act upon the starch, changing it into maltose and dextrine and the peptase to form peptones from the proteids. It must therefore be carried out under such conditions of temperature and dilution as have been found to be most favorable for effecting these purposes. We have already seen (p. 187) that the action of diastase is most effective at about 62.5° C. (144.5° F.), and therefore at a temperature not much above this is the infusion most successfully made. At a temperature of over 75° C. its power is destroyed. Two quite distinct processes for mashing are at present followed: the infusion, or thin mash, and the decoction, or thick mash, process. The first is used in England and France, the second in Bavaria, Bohemia, and the principal brewing centres of the Continent. Both are used in this country. In the infusion process, water at 60° to 70° C. is run into the mash-tub, a vessel provided with false bottom and mechanical agitation, the crushed malt added and stirred in, and then additional hotter water, so that a temperature of 70° C. (158° F.) is gradually attained. This is maintained for some time with constant agitation of the liquid, so that the diastase may have time to act upon the starch. The completion of this action is determined by taking a few drops of the wort from time to time and testing with iodine solution, which finally produces no color on mixing. The clear infusion is now run off from under the false bottom of the tub to the copper boilers, and the malt again covered with hot water and mashed for one-half to one hour longer at 70° C. or somewhat higher now. When this is run off, hot water at 200° F. is sprinkled upon the malt from a revolving "sparger" and allowed to drain off. The wort from this third mash is not always added to that of the first and second mashes, but is used to mash a fresh quantity of malt.

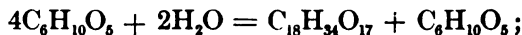
In the Bavarian thick-mash process, the malt is put in the mash-tub with some cold water, and then by the addition of boiling water is brought to 35° C. A third of the softened malt is then taken out and brought gradually to boiling with water in the copper. After one-half to three-quarters of an hour's boiling, the half of this is then returned to the mash-tub and thoroughly agitated with what remained there. The temperature of the mash-tub is thereby brought to about 50° C. A second portion of the thick mash is again taken out and boiled in the copper for three-

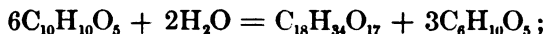
quarters to one hour, when the greater part is returned to the mash-tub and thoroughly mixed, bringing up the temperature here to 65° C. The thinner part of the mash, or clear wort, is now run off and boiled in the copper for fifteen minutes and returned, whereby the temperature of the mash-tub is brought to 75° C. This is now left at rest for an hour to an hour and a half, and then the wort is run off to the copper. The malt is washed by the sparger, and so the saccharine liquor adhering displaced. The whole process is easily understood by reference to Fig. 62, in which *A* is the mash-tub and *C* the copper for boiling up the successive portions taken from *A*.

It is obvious that in the thick-mash process that portion of the diastase contained in the material which is taken out and boiled is destroyed, but the boiling thoroughly disintegrates the malt and converts its starch into a paste. When this is returned to the mash-tub, it is very rapidly acted upon by the remaining diastase, of which there is quite sufficient, and changed into maltose and dextrine. By the thick-mash process, the sugar formation is held in check and the amount of extract increased.

In the mash process the diastase acts upon the starch of the malt, changing it into maltose and dextrin. The ratio of these products to each other changes according to the temperature used in the mashing. Moreover, as dextrin is not fermented in the main fermentation and only partially in the after-fermentation, some of it remaining in the finished beer, this matter of temperature of mashing is obviously of importance for the character of the beer.

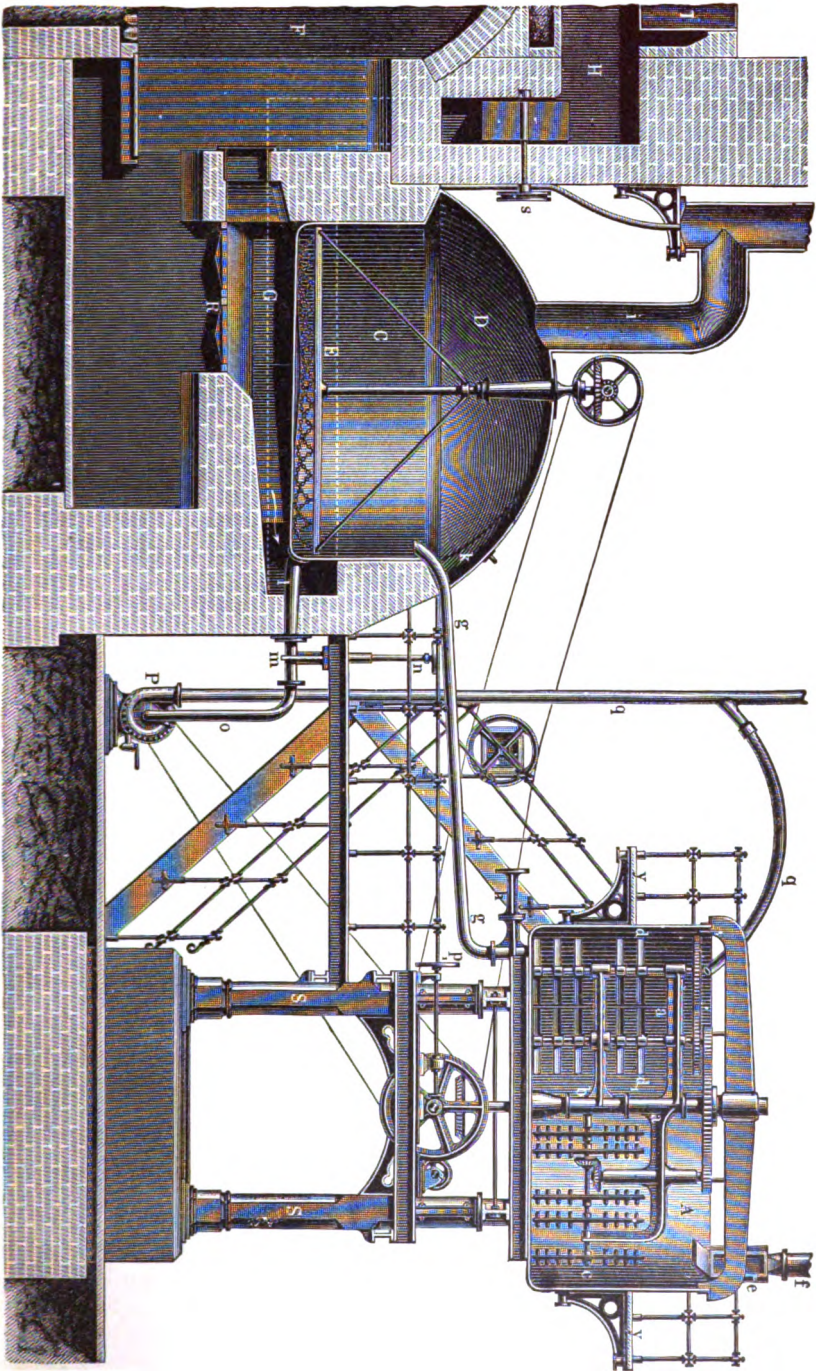
According to Märker and Schultze, at temperatures up to 65° C. the reaction takes place as follows:

$$4C_6H_{10}O_5 + 2H_2O = C_{18}H_{34}O_{17} + C_6H_{10}O_5;$$

that is, four molecules of starch react with two molecules of water to form three molecules of fermentable sugar (maltose) and one molecule of dextrin. On the other hand, at temperatures over 65° C., the reaction becomes—

$$6C_{10}H_{10}O_5 + 2H_2O = C_{18}H_{34}O_{17} + 3C_6H_{10}O_5;$$

that is, six molecules of starch react with two molecules of water to form one molecule of maltose and three molecules of dextrin.

The results of practice, at all events, show that in the infusion process, which takes place at low temperatures, beers of lower extract percentage are formed which is in part due to this difference in the production of dextrin just illustrated. A second drawback of the infusion process is that it is difficult to avoid here a larger formation of lactic acid, due to the more prolonged action of the water upon the malt, which is at just the temperature (about 50° C.) favorable for the formation of lactic acid. At the temperature of the infusion process the nitrogenous compounds are also less completely decomposed than in the decoction process, so that a beer obtained by the former process furnishes a more nutritious ground for the growth of bacterial ferments than the latter.

As the amount of diastase in the malt is sufficiently large to saccharify considerably more starch than that contained in the malt itself, at times unmalted grain and starch-containing cereals are added. The end to be attained is not only the saving of the cost of a portion of the malt, but to obtain a beer richer in extract and therefore of better keeping quality.

Fig. 62.

These malt substitutes are generally cereals rich in starch, such as corn and rice. At times unmalted barley, rye, oats, and even potatoes have also been used. Care must be taken that the saccharification in these cases of the use of corn and rice is made as complete as possible, and hence it must not be overlooked that the starch of both corn and rice requires a higher temperature (71° C.) for its complete changing into fermentable sugar. The corn or rice before use should be shelled, deprived of the germ, and crushed, so as to facilitate the liberation of its starch. The amount of malt substitute thus used should not in any case exceed thirty per cent. of the weight of the malt. In some countries, as in Bavaria, the use of malt substitutes is strictly prohibited by law.

The character of the wort is to be controlled by the use of the Balling saccharometer (see p. 163), as the specific gravity of aqueous malt extract corresponds to that of cane-sugar solutions of the same percentage strength.

3. Boiling and Cooling.—The wort is drained off from the malt-residue, or "draff," and run into the copper boiler, where it is boiled, while the hops are added at once in amount varying from one to three (or more in the case of India ales) parts to the hundred of malt, light beers taking the least amount, lager beers next, and heavy export beers the largest amount. If the amount of hops is to be calculated after the wort has been formed, 0.25 to 0.30 kilos. may be taken to the hectolitre of wort of 10 to 12 per cent., 0.40 to 0.60 kilos. to the hectolitre of wort of 12 to 15 per cent., and 0.70 to 0.80 kilos. to the hectolitre of stronger worts.

The boiling accomplishes several desirable changes in the wort: first, the protein material present is coagulated and separates out, which result is facilitated by the action of the tannic acid of the hops, which also throws out any unchanged starch; second, the wort is concentrated; third, the valuable constituents of the hops (hop-bitter and ethereal oil) are taken up by the wort and give to the beer its taste, aroma, and keeping qualities. The time of boiling varies considerably, requiring to be longer for worts prepared by the infusion process than for those by the decoction process. From one to two hours is generally sufficient where the worts do not specially need to be concentrated. Too long boiling is injurious, as the volatile oil of the hops may be lost thereby. Of one hundred parts of dry malt, sixty-five to eighty per cent. are taken up as extract in the wort; of one hundred parts of hops, twenty to thirty parts.

The wort is now to be cooled preparatory to the fermentation. This cooling must be effected as rapidly as possible, so that the lactic fermentation and similar changes may not take place. The cooling is generally effected in very shallow wide tanks, which are placed where a good circulation of air can be assured. From these tanks the still warm wort is often run through a circuit of pipes cooled by ice-water flowing around them, or is run in thin streams (known as a "beer fall') over a series of pipes through which cold water or chilled brine from the refrigerating apparatus circulates. Such an arrangement is now coming into extensive use in large breweries provided with artificial refrigeration. Of course, in such a method of cooling the wort is exposed for a considerable time to impure air containing spores, which, getting into the liquid, may afterwards affect the fermentation. In all cases where Hansen's pure yeast is to be employed the wort must be cooled in vessels to which only sterilized air has access. For an arrangement of this kind, see Wagner's "Chemical Technology," 13th ed., p. 911.

It is thus cooled down to the point needed for the beginning of the fermentation. This point depends upon the character of the fermentation, whether with top yeast or bottom yeast; for the latter it must be some 8° to 10° C. below that needed for the former. The cooled wort is now allowed to deposit a sediment of coagulated albuminoids, particles of hops, etc., which were suspended in it when the cooling began. This sediment is gathered and pressed and the liquid added to the rest of the wort.

4. FERMENTATION OF THE WORT.—The wort may either be left to spontaneous fermentation depending upon the spores of yeast ferments, which are always present in the air of a brewery, or it is started into fermentation by the addition of yeast. The former method is followed in Belgium, but in the great majority of cases elsewhere fermentation is incited by the direct addition of a suitable yeast. As stated before in the section on the nature of fermentation (see p. 185), there are two radically different methods of carrying out this process in practice: the surface fermentation and the bottom fermentation. The first of these, followed almost exclusively in England for all malt liquors and in this country for ales, is specially adapted for worts rich in maltose, and takes place more rapidly, at a higher temperature, and produces more alcohol. As English worts, moreover, are usually prepared by the infusion method, a considerable quantity of soluble gluten is left in the liquor, which on exposure to the air, as in half-empty casks, may start the acetic fermentation, or souring. The second of these, followed in Germany and Austria and in this country for lager-beer, proceeds more slowly; the production of alcohol is restrained by the low temperature, and as the fermentation proceeds with freer and more prolonged access of air, the yeast-plants in their growth consume the proteid matter as food. Consequently there is less albuminoid matter left to start souring, and the beer is a better-keeping beer than those prepared by the more rapid surface fermentation. Of course, the proportion of malt and hops used and the alcohol percentage also come into consideration in the matter of keeping quality, and may offset the advantage just mentioned. The fermentation, by whichever method carried out, may be divided into three stages: first, the *main fermentation*, which begins shortly after the addition of the yeast, and is specially characterized by the decomposition of maltose, the formation of new yeast-cells, and the rise of temperature; second, the *after-fermentation*, in which the decomposition of maltose still continues, but the formation of yeast-cells has nearly ceased, and the yeast particles suspended in the beer settle out and the beer clears; and, third, the *still fermentation*, which follows the completed after-fermentation, in which maltose is still decomposed and some dextrine is changed into maltose by what diastase is present, but the yeast-cells are no longer formed.

The fermenting vessels are great oaken tuns holding fifty to one hundred barrels. The thick froth, or magma, of yeast is added in amount varying from one-half to three-quarters of a litre per one hundred litres of wort of ten to fourteen per cent. It may either be added direct to the whole body of the wort and stirred in, or may be mixed with a smaller amount of the wort, allowed to stand for four to five hours until fermentation starts, and then the mixture added to the main body of the wort. In the surface fermentation process, the main fermentation lasts from four to eight days, during which time the temperature must be carefully regulated and held at from 14° to 18° C. The surface is at first covered with a white foam which rises, and curls and breaks into a variety of forms. The

temperature rises from two to four degrees, and care must be taken to control and reduce this, which used to be done by the use of conical cans, or "swimmers," holding ice, floated at the top of the tun, cooling the mass, but the tuns are now cooled just as the fermenting cellars are, by artificial means. The fermentation is not allowed to go to completion at this initial temperature, but the beer is transferred for the after or slower fermentation to cooler cellars (of about 5° C.), where it is put into storage-casks. After sufficient time here, it is drawn into casks containing beechwood shavings, to which isinglass is sometimes added to clear it, and there is added to it some fresh fermenting beer ("Kräusen"), in the proportion of one barrel to twenty, which starts a new fermentation, giving the beer its "head." In the bottom fermentation, the fermenting cellar is kept at 4° to 5° C., and the main fermentation lasts from nine to ten days. The after-fermentation follows in cellars cooled to 1° to 2° C., and lasts correspondingly longer.

Berlin weiss-beer is brewed from malted wheat to which some malted barley is added, and is fermented at relatively higher temperature (16° to 24° C.). At the end of the main fermentation, which is finished in three days, it is transferred, with the addition of some fresh fermenting beer, to tightly-stopped stone jugs, in which the after-fermentation takes place. In eight to fourteen days it is in condition for drinking. It is, of course, effervescing, is somewhat turbid, and has a sour taste from lactic acid which has formed.

5. Preservation of Beer.—Beer or ale intended for export may of course have keeping qualities imparted to it in its manufacture by special addition of hops, or otherwise, but most beers can have their keeping qualities improved by direct treatment after they are finished beverages. This is most legitimately done by the process of "Pasteurizing," which consists in heating the beer either already bottled or in casks to a temperature of about 60° C., which apparently kills all ferments which develop the souring of beer. Less legitimate and forbidden by law in many countries is the addition of salicylic acid, boric acid, or calcium bisulphite.

## III. Products.

The various designations that have been given to malt liquors do not necessarily imply distinctive differences in the character of the product. They represent largely the different usages of different countries and localities. Thus, in England *Ale* was at one time brewed without hops, but the term now is applied to a beer brewed by the surface fermentation process, which is practically the only method used in England. *Porter* has now come to mean a dark malt liquor, made partly from brown or black malt, the caramel in which gives it the sweetness and syrupy appearance, and containing four or five per cent. of alcohol. *Stout* is a stronger porter, with larger amount of dissolved solids, and containing six or seven per cent. of alcohol.

*Lager-beer* is beer as brewed in Germany by the bottom fermentation process, which process is, moreover, retarded, so that the beer has better keeping qualities. It also has a larger amount of hops used in its production. It is brewed in winter for storage and use in summer. *Schenk-beer* is also a bottom fermentation beer, but is designed for use as soon as finished, and the process is somewhat quicker than with lager-beer, and a smaller

amount of hops is used. *Bock-beer* is a stronger lager-beer, made with one-third more malt, and brewed specially in the spring of the year. *Weiss-beer*, as before stated, is made chiefly from malted wheat, and is yet in the after-fermentation. Most other names are from localities, and represent the characteristic products of those places.

The composition of various English and German beers is given in the accompanying table on the authority of Professor Charles Graham. (Allen, Commercial Organic Analysis, 2d ed., vol ii. p. 92.)

| | Maltose. | Dextrine. | Albuminoids. (Wanklynized.) | Ash, coloring, etc. | Total solids. | Acetic acid. | Lactic and succinic acid. | Alcohol. | Ratio of solids to alcohol. |
|---|---|---|---|---|---|---|---|---|---|
| Burton pale ale . . . . | 1.75 | 2.48 | 0.21 | 0.55 | 5.13 | 0.02 | 0.14 | 5.37 | 1:1.05 |
| Burton bitter ale . . . . | 1.62 | 2.60 | 0.16 | 0.87 | 5.42 | 0.01 | 0.17 | 5.44 | 1:100 |
| Mild X . . . . . . . . . | 1.87 | 1.88 | 0.20 | 1.30 | 5.39 | 0.04 | 0.14 | 4.60 | 1:0.85 |
| XXX . . . . . . . . . | 2.88 | 2.04 | 0.30 | 1.48 | 6.80 | 0.02 | 0.10 | 6.50 | 1:0.96 |
| Scotch export, bitter . . | 1.62 | 2.50 | 0.30 | 0.70 | 5.21 | 0.16 | 0.09 | 5.00 | 1:0.96 |
| Dublin stout, XX . . . | 3.45 | 3.07 | 0.26 | 1.76 | 8.71 | 0.01 | 0.17 | 5.50 | 1:0.63 |
| Dublin stout, XXX . . . | 5.35 | 2.09 | 0.43 | 1.40 | 9.52 | 0.04 | 0.25 | 6.78 | 1:0.71 |
| Vienna lager . . . . . . | 1.64 | 2.74 | 0.36 | 1.12 | 5.90 | 0.02 | 0.13 | 4.69 | 1:0.78 |
| Pilsen lager . . . . . | 0.69 | 2.65 | 0.20 | 0.59 | 4.22 | 0.02 | 0.09 | 3.29 | 1:0.80 |
| Munich lager . . . . . | 1.57 | 3.15 | 0.40 | 1.82 | 7.08 | 0.01 | 0.14 | 4.75 | 1:0.67 |

The composition of various American beers and ales as analyzed by C. A. Crampton, of the United States Department of Agriculture, is also given.*

| | Maltose. | Dextrine. | Albuminoids. | Free acids as lactic. | Ash. | Phosphoric acid. | Extract. | Alcohol. | Specific gravity. |
|---|---|---|---|---|---|---|---|---|---|
| Milwaukee lager, bottled . . . . | 1.10 | 1.57 | 0.51 | 0.057 | 0.196 | 0.065 | 4.18 | 4.28 | 1.0100 |
| Milwaukee export beer, bottled . | 1.06 | 2.63 | 0.40 | 0.057 | 0.309 | 0.056 | 5.40 | 4.42 | 1.0140 |
| Milwaukee "Bohemian" beer . . | 1.82 | 3.04 | 0.406 | 0.071 | 0.224 | 0.057 | 5.88 | 4.16 | 1.0183 |
| Milwaukee "Bavarian" beer . . | 1.75 | 2.87 | 0.556 | 0.074 | 0.346 | 0.077 | 6.26 | 5.06 | 1.0187 |
| St. Louis export beer . . . . . | 2.14 | 2.54 | 0.463 | 0.067 | 0.312 | 0.074 | 6.15 | 4.40 | 1.0178 |
| St. Louis pale lager, bottled . . . | 2.17 | 2.75 | 0.463 | 0.067 | 0.312 | 0.064 | 4.64 | 4.28 | 1.0178 |
| St. Louis "Erlanger" beer, bottled | 2.51 | 2.58 | 0.675 | 0.046 | 0.183 | 0.093 | 6.82 | 4.68 | 1.0203 |
| Philadelphia lager, bottled . . | 1.46 | 2.30 | 0.538 | 0.086 | 0.241 | 0.078 | 5.22 | 4.29 | 1.0147 |
| Philadelphia "Budweiss," bottled | 2.14 | 2.57 | 0.531 | 0.046 | 0.265 | 0.095 | 5.94 | 4.52 | 1.0181 |
| Philadelphia ale, bottled . . . . | 0.59 | 0.90 | 0.531 | 0.232 | 0.401 | 0.085 | 3.46 | 6.24 | 1.0059 |
| Reading ale, bottled . . . . . . . | 0.93 | 1.99 | 0.731 | 0.382 | 0.472 | 0.077 | 5.55 | 6.92 | 1.0125 |
| Reading porter, bottled . . . . . | 2.67 | 2.88 | 0.763 | 0.166 | 0.412 | 0.100 | 8.19 | 4.89 | 1.0269 |

## IV. Analytical Tests and Methods.

1. For Malt.—The brewing value of a sample of malt is dependent upon three factors,—namely, the proportion of soluble or extractive matter it will yield to water; the character of this extractive matter; and the diastatic activity. The extractive matter in malt is usually determined by a miniature mashing processs. This is carried out as follows:† The malt is first crushed uniformly fine; fifty grammes are then weighed out as rapidly as possible (on account of its hygroscopic character), and placed in a weighed

* United States Department of Agriculture, Bulletin No. 13, Part iii. p. 282.
† Allen, vol. ii. p. 269.

beaker with two hundred and fifty centimetres of distilled water at 50° to 52° C. After a short digestion at this temperature, the heat is gradually raised to 59° or 60° C., and this temperature maintained until a drop taken from the liquid cease to give a blue color with iodine solution and nearly ceases to give a brown. The heat is then increased to about 70° C. in order to complete the saccharification, when the water in the bath surrounding the beaker is boiled for five minutes. The beaker is then cooled and the contents filtered. The insoluble matter is washed with cold water, and the filtrate is made up exactly to four hundred cubic centimetres. The density of the clear wort is next taken at 15.5° C. (60° F.) by a specific gravity bottle. For most purposes, it is sufficiently accurate to make up the unfiltered wort to four hundred and fifteen cubic centimetres, filter a portion through a dry filter and take the density. The draff is here assumed to measure fifteen cubic centimetres, and the tedious washing is dispensed with. The excess of density over that of water (taken at 1000) multiplied by 2.078 will give the percentage of dry extract yielded by the malt. This method is based on the fact that each gramme of malt extract per hundred cubic centimetres of infusion has been shown by experiment to raise the density of the liquor by 3.85 degrees (water = 1000). The figure 2.078 is then the fraction $\frac{8}{3.85}$. Instead of ascertaining the gravity of the infusion, the proportion of solid matter may be determined by evaporating a known measure of the wort to dryness in a flat-bottomed dish so that the residue may form a thin film. This is dried at 105° C. and weighed. Other methods are those of Metz,* with the use of Schultze's tables, and of Metz as improved by Weiss.

The determination of diastatic power in a sample of malt is also of importance in valuing it, even if the full diastatic power is not likely to be called out in the brewing process, where it is usually in excess of the need for the production of a beer-wort. The older process of Lintner† depended upon determining by the aid of Fehling's solution the amount of maltose produced by the action of a cold infusion of the malt upon a measured starch solution. This, however, supposes that the action of diastase upon starch in the cold is always uniform and produces the same relative amount of maltose, which is now regarded as a matter of some uncertainty. The method proposed by Dunstan (Allen, 2d ed., vol. ii. p. 278) simply notes the end of the transformation of the starch by the absence of color with iodine solution. For it five grammes of very finely-powdered malt are digested and agitated for one hour with fifty cubic centimetres of cold water. The liquid is then strained off and the residue again digested for an hour with fifty cubic centimetres of water, and the liquids are then mixed and made up to one hundred cubic centimetres. Five-tenths gramme of starch (dried at 100° C. before weighing) is gelatinized by boiling with water, and the cold liquid diluted to one hundred cubic centimetres. The solution of malt extract is then added to twenty cubic centimetres of this mucilage by instalments of one cubic centimetre, at intervals of half an hour, until it ceases to give any color, when a small quantity is tested with a dilute solution of iodine. If less than one cubic centimetre of the solution produces this effect, more of the mucilage should be added and the operation continued.

To determine the soluble proteids of malt assumed to represent the

* Stohmann and Kerl, Technische Chemie, 4th ed., pp. 1345–1351.
† Lintner, Die Bierbrauerei, p. 530.

diastase C. Graham proposes to use the Wanklyn albuminoid-ammonia process.

2. FOR BEER-WORTS.—The determination of the specific gravity of the wort is of importance, as from this may be calculated the total solid matter in the wort. If from the specific gravity of the wort we take 1000, and divide the difference by 3.85, we get the number of grammes of solid extract contained in one hundred cubic centimetres of the wort. For the purpose of the brewer special forms of hydrometers have been constructed, the readings of which are immediately available. Thus, Bates's saccharometer gives readings of pounds per barrel (of thirty-six gallons),—that is, excess of weight in pounds of a barrel of wort over the same bulk of water. These readings can then be converted into real specific gravity figures by a simple proportion, using the weight of a barrel of pure water, of this wort with the excess of weight shown by the saccharometer reading and the specific gravity of pure water as terms. The Bates saccharometer readings can be converted into those of Balling or Brix by the following formula: Balling $= \frac{260 \text{ Bates}}{360 + \text{Bates}}$. The method of ascertaining the original gravity of beer-worts which have undergone fermentation is described later. (See following page.)

In brewing, the relative proportion of maltose and dextrine in the wort is of great importance and is liable to considerable variation, being dependent on the temperature at which the mashing was conducted, the length of time occupied in the process, and the diastatic activity of the malt employed. The composition of the wort largely influences the subsequent fermentation, as a wort containing little dextrine will produce of beer of low density which will clarify readily, but be "thin" and apparently much weaker than beer of the same original gravity but higher final attenuation. C. Graham estimates the maltose and dextrine in beer-worts from the cupric oxide reducing power of the solution before and after inversion. (For details of his procedure, see Allen, vol. ii. p. 274.) West Knight (Analyst, vii. p. 211) has described a very simple and rapid method of approximately determining the dextrine in beer-worts. Ten cubic centimetres of the wort is treated in a small weighed beaker with fifty cubic centimetres of methylated spirit of .830 specific gravity. This causes the precipitation of the greater part of the dextrine, which after a few hours collects on the bottom of the beaker as a gummy mass, from which the alcoholic liquid can be poured off. The deposit is rinsed with a little more spirit, and the beaker dried in the water-oven and weighed. To the weight obtained an addition of .045 gramme is made as a correction for the dextrine retained in solution by the spirituous liquid.

3. FOR BEER.—The *specific gravity* of the beer is a determination that is necessary as a basis of calculation for the other determinations as to its composition. It should be made after freeing the beer from carbon dioxide as fully as possible. It can be made with a specific gravity flask, but is most readily and accurately carried out with a Westphal specific gravity balance (see Fig. 33), which for this purpose is provided with a fourth rider giving the fourth place of decimals.

The amount of *extract* is frequently determined by taking a definite volume of beer of which the specific gravity has been determined, evaporating it to one-third its bulk, and then adding water sufficient to restore it to original bulk. The specific gravity of this liquid is then determined as just described.

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The percentage of extract can now be found by a reference to Schulze's tables for determining the amount of extract by specific gravity, or more simply by O'Sullivan's method, in which the excess of this specific gravity over 1000 divided by 3.86 gives the number of grammes of dry extract per one hundred cubic centimetres of the beer. C. Graham considers it decidedly more accurate to evaporate five cubic centimetres of the beer on a flat watch-crystal in an air-bath at a temperature of from 70° to 75° C. The complete drying of the film requires about twenty-six hours.

The percentage of *alcohol* is best determined by distillation. For this purpose one hundred cubic centimetres of the beer are taken, a few drops of caustic soda added to neutralize the free acid, and the liquid brought up to about one hundred and fifty cubic centimetres. It is then distilled with the aid of a Liebig condenser into a graduated flask until nearly one hundred cubic centimetres have come over. The distillate is now thoroughly mixed, cooled to 15° C., and then brought exactly to the 100-cubic-centimetre mark and again mixed. Its specific gravity is now taken, and from a set of alcohol tables (see Hehner's tables, Appendix, p. 522) the percentage of alcohol by weight of the distillate found. Then as the specific gravity of the original sample is to the specific gravity of the distillate so is the weight per cent. in the distillate to the weight per cent. in the original sample. Indirectly the alcohol percentage can be determined, although not with the same accuracy, by the aid of the data gotten in the determination of extract already narrated. For if the specific gravity of the original sample be divided by the specific gravity of the de-alcoholized solution we get the specific gravity of the alcohol driven off, from which figure the percentage by weight of alcohol can be gotten in the tables. When both the alcohol and the extract percentage of a beer are known, by Balling's method the percentage of *extract in the original wort* can be calculated, and then with the aid of this and the percentage of extract in the beer the "attenuation" or diminution in the gravity of the original wort due to fermentation and alcohol production can be determined. As the weight of alcohol produced is approximately fifty per cent. of the saccharine matter destroyed by the fermentation, we have the formula $2a + e = w$, in which $a$ is the alcohol percentage, $e$ the extract percentage of the beer, and $w$ the percentage strength of the original wort. Then using this figure just obtained $w : 100 :: 2a : x$, in which $x$ will represent the degree of attenuation. More accurately, the actual degree of fermentation (*Wirklicher Vergährungsgrad*) is gotten by the proportion $p : p - n :: 100 : v'$, in which $p$ is the extract in the original wort, $n$ the extract in the beer, and $v'$ the actual fermentation degree; $(p - n)$ is termed the "real attenuation." It is obvious from the two proportions given that in practice $2a$ is often taken as equivalent to $(p - n)$. This is not strictly correct. It is found in the fermentation of beer-worts that 100 parts of extract yield 48.391 parts of alcohol, so that what is termed an "alcohol factor" is necessary to convert one into the other. In England a different procedure is followed. A definite volume of beer is taken and one-half distilled off. This distillate is brought up with water at 60° F. to the original volume and its specific gravity taken. The difference between 1000 and the observed gravity is called the "spirit indication" of the beer. With this can be found, in a table prepared for the Inland Revenue Office, the "degrees of gravity lost" by the attenuation of the wort. Then the liquid left in the retort after the distillation is diluted with water and brought up to the original volume, when its specific gravity is

carefully taken. This is called the "extract gravity," and this added to the degrees of gravity lost gives the "original gravity of the wort."

The *acidity* of beer is partly due to lactic and succinic acids, which are fixed acids, and partly to acetic acid, which is volatile. The fixed acids are usually determined jointly in terms of lactic acid by dissolving the dry extract of the beer in water and titrating the solution with decinormal alkali solution. Baryta-water is preferred by many chemists, as the sulphate of baryta which forms carries down much of the coloring and allows the end reaction to be better seen. The volatile acid of beer is chiefly acetic acid, which is usually determined by subtracting the measure of alkali required to neutralize the extract from that required by the original beer (after getting rid of the carbonic acid by shaking thoroughly).

The chief *adulterations* of beer are from the use of salicylic acid as a preservative and the addition of various bitter principles as substitutes for hop-bitters. The salicylic acid may be searched for by concentrating the beer to one-half at a gentle heat and shaking the cooled liquid with ether, or a mixture of ethylic ether and petroleum-ether. The ethereal layer is then separated, evaporated to dryness, and the residue dissolved in warm water. On adding ferric chloride, a violet coloration is produced if salicylic acid be present. Other chemists recommend dialyzing, when the salicylic acid will readily dialyze into the pure water and can then be tested. For the detection of the bitter principles used as substitutes for hops elaborate schemes have been proposed by Enders (given in Allen, vol. ii. p. 97) and Dragendorff (Gerichtliche-Chemische Ausmittelung der Gifte).

## C. THE MANUFACTURE OF WINE.

### I. Raw Materials.

1. THE GRAPE.—While the name wine is often used to include the products of the spontaneous alcoholic fermentation of any sweet fruit or berry, it is usually limited to the product of the fermentation of the grape, which alone is cultivated on an extensive scale throughout the civilized world purely for the manufacture of wine.

The cultivation of the grape-vine and the production of wine therefrom dates back to the earliest historic times. Beginning in the East and the Mediterranean lands, it extended northward and westward until at present France is the chief wine-producing country, while Germany, Austria, Spain, and Portugal have all established flourishing wine industries indigenous to their soil. In this country, the wine industry is mainly established in the States of Ohio, New York, Virginia, and California.

The varieties of the vine (estimated to number almost two thousand) hitherto cultivated in Europe are all said to be derived from the single species, *Vitis vinifera*. In this country four or five wild species have yielded varieties which when cultivated have proven adapted to wine production. Thus *Vitis riparia*, or "frost-grape," has yielded as cultivated varieties the Taylor and the Clinton grapes; the *Vitis æstivalis*, or "summer-grape," has yielded as varieties Norton's Virginia, Cythiana, and Herbemont; the *Vitis Labrusca*, or "Northern fox-grape," has yielded as varieties the Catawba, Isabella, Concord, and Delaware grapes; the *Vitis vulpina* or *rotundifolia*, or "Southern muscadine," has yielded as varieties the black, red, and white Scuppernong. Numerous varieties of the European vine, the *Vitis vinifera*,

have also been cultivated successfully in California, among which may be mentioned the Mission, Riesling, Traminer, Rulander, Gutedel, and Zinfandel.

The grapes owe their wine-producing value in the first place to the grape (or invert) sugar which they contain, and in the second place to the free acids, which in the later ripening of the wine are to develop the fragrant ethers, and to the albuminoids, which exert a great influence on the fermentation. The composition of the grape varies of course in different localities and even from year to year in the same locality, but its mean composition is thus stated by König: Grape-sugar, 14.36 per cent.; free acid (tartaric), .79 per cent.; nitrogenous material, .59 per cent.; non-nitrogenous extract, 1.96 per cent.; skins and kernel, 3.60 per cent.; ash, .50 per cent.; and water, 78.17 per cent.

The grapes are taken for wine-making only when they are fully ripe, and in many localities it is even customary to wait until the grape shows a slight appearance of over-ripeness or evidence of wilting, so that the maximum of sweetness may be attained. In some cases the grapes are plucked from the stems, either by hand or by the aid of three-pronged forks, while in other cases the stems are left when they are crushed in order that the tannin so obtained may aid in the clearing of the fermenting juice. This juice is known as "must," and the pressed pulp and skins as the "marc."

2. The Must.—This may properly be considered as still a raw material, as its expression from the grapes is purely a mechanical process. This is now generally effected by power-presses of various forms, although at one time largely effected by trampling the grapes under feet. (This method is still followed in the Oporto and the Madeira wine districts.) The first portion of must that runs from the presses is often collected separately, as it is the juice of the ripest and sweetest grapes; that which comes later is richer in acid and in tannin, as it comes partly from unripe grapes and partly from the stems and skins. The amount of must that is obtained usually ranges from sixty to seventy parts in the one hundred of grapes.

The composition of this must is of the greatest importance, as upon it depends the character of the wine that will be produced, whether it shall ferment normally throughout and develop the perfect flavor and aroma desired, or whether it shall be thin and sour and show tendencies towards alteration or "disease." The proportions of its constituents, especially the grape-sugar, may vary within quite wide limits from year to year, and in grapes grown in the same year under different conditions of soil, exposure, etc.

Thus, two different musts of 1868 are given and two musts of the same variety of grape in two succeeding years, the first of which was a favorable year and the second an unfavorable year. The analyses are all by Neubauer.

| | Sugar. | Free acid. | Albuminoids. | Ash. | Non-nitrogenous extract. | Water. |
|---|---|---|---|---|---|---|
| Neroberger Riesling, 1868 . . . . . . | 18.06 | 0.42 | 0.22 | 0.47 | 4.11 | 76.72 |
| Steinberger Auslese, 1868 . . . . . . | 24.24 | 0.43 | 0.18 | 0.45 | 3.92 | 70.78 |
| Hattenheimer, 1868, (good year) . . . | 23.56 | 0.46 | 0.19 | 0.44 | 5.43 | 69.92 |
| Hattenheimer, 1869, (bad year) . . . | 16.67 | 0.79 | 0.33 | 0.24 | 5.17 | 76.80 |

The percentage of grape-sugar in the must sinks at times to twelve per cent., and may rise as high as twenty-six to thirty per cent. The ratio

between acid and sugar, according to Fresenius, ranges from 1 : 29 for good varieties of grapes in good years to 1 : 16 for inferior varieties in medium years. If the ratio falls as low as 1 : 10, the grapes are unripe and taste acid. This ratio of acid to sugar is now generally taken as the criterion for the quality of the must in any year or special locality.

In bad seasons the free acid is more generally malic than tartaric, which is the normal constituent.

## II. Processes of Manufacture.

1. FERMENTATION.—The fermentation of the must is a spontaneous one following exposure to the air, and due to the spores which drop upon the surface of the must as exposed in the fermenting-tubs. It may be a surface fermentation, taking place at temperatures of 15° to 20° C., as is the practice in Italy, Spain, and the south of France, or a bottom fermentation, taking place in cooler cellars at 5° to 12° C., as is the practice in Germany and with the finer French wines. The first method produces a fiery wine rich in alcohol, but without bouquet or aroma; the second method, lighter wines with delicate bouquet, due to the formation of wine ethers. In either case the fermentation can be divided, as was the case with malt liquors, into three stages: the first, or main fermentation, which, according as the surface or the bottom fermentation method is followed, lasts from three to eight days, or from two to four weeks; the second, or still fermentation, which lasts until the following spring; and the third, the storage fermentation, which lasts for several years, until by the gradual development of its bouquet it becomes perfectly ripe.

In the case of red wines, the main fermentation is allowed to take place with the marc added to the must, so that as the alcohol is developed it may dissolve out the coloring matter (œnocyanin) of the skins as well as some of the tannin, which latter is of benefit in effecting a more rapid separation of the protein materials. To prevent this pulpy mass from rising to the surface and starting a souring of the wine, perforated covers are often used in this case to hold it down. In the main fermentation, the casks are usually freely exposed to the air Many wine experts recommend in addition the aeration of the fermenting must or a whipping of the liquid, so as to induce a fuller and more vigorous fermentation On the other hand, other authorities consider that this excessive exposure to air injures the quality and aroma of the wine, and recommend only a partial exposure to the air after the main fermentation has begun. As the main fermentation comes to an end, the yeast (with more or less tartar, gummy matter, and albuminoids) settles to the bottom, the liquid clears and is ready to be racked off into casks, under the name of *young wine* (Jungwein), to undergo the after- or still fermentation. If the racking off does not take place promptly with the ending of the more energetic main fermentation, the young wine, of which a considerable surface is exposed to the air, is very apt to start into the acetic fermentation. The casks into which it is now put are kept quite full in order to prevent this undesirable change, slight additions being made every few days if necessary, and the bungs are set loosely in place. During this after-fermentation there deposits upon the inner walls of the cask *argols*, or impure acid potassium tartrate (Weinstein), with some yeast and albuminoid matter. This fermentation lasts from three to six months, and then the wine is racked off again into smaller

casks to undergo the final ripening, in which the bouquet of the wine is especially developed by the formation of ethers, while it clears more thoroughly from the remaining particles of yeast, etc. The duration of this ripening may be two, four, or with rich wines even eight years or more, when it is considered "bottle-ripe." During this ripening fungous vegetation is very apt to start, and must be arrested in order to prevent the spoiling of the wine.

2. DISEASES OF WINES AND METHODS OF TREATING AND IMPROVING THEM.—The souring of wine, due to the beginning of the acetic fermentation, is one of the commonest of these so-called diseases, especially with light wines, poor in alcohol and tannic acid, and hence commoner with white than with red wines. It arises from too free an exposure to the air and too high a temperature during fermentation. If just begun, it can be cured by the addition of a small quantity of potashes, which form potassium acetate, or by starting the alcoholic fermentation afresh by adding a new quantity of sugar. If the souring is very pronounced it cannot be cured, and the wine is made into wine-vinegar.

The gumminess or ropiness of wine frequently arises from a premature filling into bottles, and is due to the beginning of the mucous fermentation of sugar. It takes place in wines poor in tannic acid, and hence more readily with white than with red wines. It can be cured by addition of tannic acid, treatment with sulphurous oxide, or starting a new fermentation by addition of grape-sugar.

The development of a stale or flat taste in the wine is due, according to Pasteur, to the growth of a thread-like ferment. The wine becomes cloudy, diminishes in alcohol and increases in acid percentage, it darkens in color, and often has a disagreeable odor. The wine is racked off and put into a cask which has been filled with sulphurous oxide fumes, which destroy the ferment.

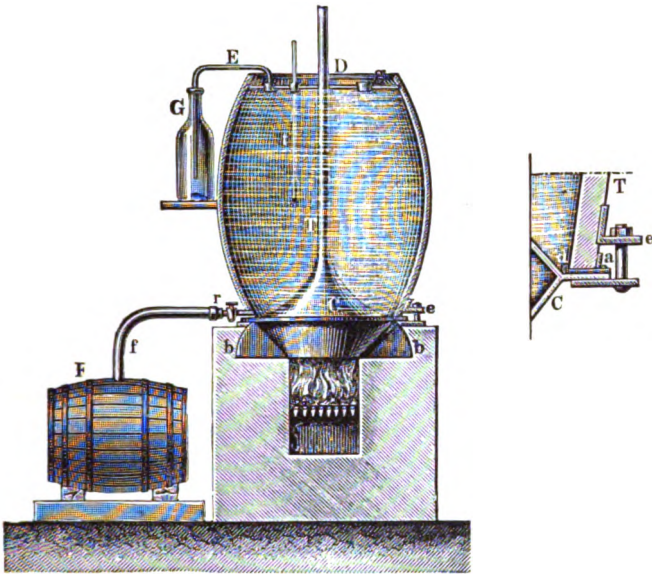
The turning bitter of red wines is due also, according to Pasteur, to a plant-growth, according to others to the formation of a bitter aldehyde resin. Neubauer has found that the tannic acid and the coloring matter both decrease in percentage in this disease. It can be cured completely by heating the wine to 60° to 64° C., or by starting the fermentation anew by adding fresh quantities of grape-sugar.

The mouldiness of wine is due to the development of a fungoid growth in the form of a white film on the surface of wines poor in alcohol, and always precedes the souring of the wine. It is to be obviated by treatment with sulphur dioxide or more effectual protection of the young wine from the air.

Of the general lines of treatment adopted to prevent the development of these various diseases, we notice first the clarifying with isinglass (finings) or other form of gelatine. This is particularly applied to the sweet and heavy white wines, which often remain turbid and have to be cleared by the coagulating of the albuminoid which is added. With red wines which contain tannic acid, casein or blood albumen is used instead of gelatine. Fine clays are also used, especially in Spain, for this clarifying.

The most important process, however, which is applied for the preservation and protection of wine against diseases is that known as "Pasteurizing." It consists in heating the wine either in casks or in bottles to a temperature of 60° C., and then preserving it without exposure to the air.

This temperature is found to be sufficient to kill most of the germs which bring about the diseases before mentioned. A form of cask much used for this "Pasteurizing" process is shown in Fig. 63.

FIG. 63.

The use of salicylic acid for preserving wines has been extensively tried, but its use here is open to the same objection as before stated in speaking of beer, and it is now forbidden in most countries.

Of the methods of "improving" wines, as it is termed, that known as "plastering" is probably most largely practised, its use for red wines extending to Spain, Portugal, Italy, and the South of France. It consists in adding plaster of Paris (burnt gypsum) either to the unpressed grapes or to the must. The plaster takes up water and so increases the alcoholic strength of the fermenting must, which in turn allows of a greater extraction of the coloring matter from the skins. At the same time the wine is given better keeping qualities as well as deeper color. However, the sulphate of lime changes the soluble potash salts of the wine into insoluble tartrate of lime and soluble acid sulphate of potash, which latter remains dissolved along with some of the gypsum, and undoubtedly has an injurious effect upon the consumers of the wine. The process has hence had to be controlled by law, and in France the sale of wine containing over .2 per cent. of potassium sulphate is prohibited. The ash of pure wine does not exceed .3 per cent., but in the samples of sherry usually met with it reaches .5 per cent., and is almost entirely composed of sulphates.

Hugonneng recommends adding dicalcium phosphate instead of gypsum. This process, called "phosphotage," is said to have all the good effects obtainable from plastering without increasing, as the latter does, the percentage of sulphuric acid and decreasing that of phosphoric acid.

Chaptalization consists in neutralizing the excess of acidity in the must by the addition of marble-dust, and increasing the saccharine content by

the addition of a certain quantity of cane-sugar, which the vintners sometimes replace by starch-sugar. In this process the quantity of the wine is not increased, but it becomes richer in alcohol, poorer in acid, and the bouquet is not injured. It is much used in Burgundy.

Gallization, as proposed by Dr. Gall, has for its object the bringing of the must of a bad year up to the standard found to belong to a good must (he takes as standard 24 per cent. of sugar, .6 per cent. of acid, and 75.4 per cent. of water) by correcting the ratio of acid to sugar. This he does by adding sugar and water in sufficient quantity, and tables have been prepared to indicate the quantity needed according to the acid ratio shown by analysis. In both these processes, starch-sugar ought never to be used as a cheaper substitute for cane-sugar, as commercial starch-sugar will always introduce dextrine, an entirely foreign constituent, into the must.

Petiotization is a process which takes its name from Petiot, a proprietor in Burgundy, and is carried out as follows: The marc from which the juice has been separated as usual by pressure is mixed with a solution of sugar and water and the mixture again fermented, the second steeping containing, like the first, notable quantities of bitartrate of potash, tannic acid, etc., which are far from being exhausted by one extraction. The process may be repeated several times, the different infusions being mixed. This process is very largely used in France, and is said to produce wines rich in alcohol, of as good bouquet as the original wine, and of good keeping qualities. It is not allowed to be sold there, however, as *natural* wine.

Scheelization consists in the addition of glycerine to the finished wine so as to improve the sweet taste without injuring its keeping qualities. The limits of the addition of glycerine lie between one and three litres to the hectolitre of wine. If the wine has not fully fermented, however, and if yeast-cells are present, the glycerine may yield propionic acid by decomposition.

3. MANUFACTURE OF EFFERVESCING WINES (*Champagnes*).—For the manufacture of champagne the blue sweet grapes are preferred. They must be pressed promptly after picking in order that the least possible amount of color be taken up by the must. The first pressing only is used for the champagne, and a second pressing of the marc yields a reddish wine, which is differently utilized. The must is first put into vats that impurities may settle and then filled into casks for the main fermentation, which is retarded as much as possible by being carried out in cool cellars. Cognac is also added to the amount of about one per cent., so as to increase the alcohol percentage and thus moderate the fermentation. After the main fermentation is finished the wine is racked off into other casks and left stopped until winter (end of December). It is then fined (or cleared) with isinglass and transferred to other casks, and this operation is repeated in a month's time. Towards the beginning of April it is ready to be transferred to bottles. The wines of different growths are now mixed and the amount of sugar in the wine determined, when a calculated additional quantity is added in the form of "liqueur" (a mixture of alcohol and pure cane-sugar). The bottles which are to receive the champagne must be specially chosen and be sufficiently strong to stand the pressure, which rises later to four to five atmospheres. They must also have sloping sides, so that the sediment may not adhere to the sides in the after-process. The wine after being corked is thoroughly secured by an iron fastening called an *agrafe*, and the bottles are arranged in piles in a horizontal position in the large champagne-vaults, where they

remain throughout the summer months. Previous to the wine being prepared for shipment, the bottles are placed in a slanting position, neck downward, in frames, and the incline is gradually increased day by day until the bottle is almost perpendicular. With the sediment thus on the cork it goes into the hands of a workman called a "disgorger," who, holding the bottle still neck downward, proceeds to liberate the cork by slipping off the agrafe, and when the cork is three-fourth parts out he quickly inverts the bottle. The cork is thus forcibly ejected with a loud report by the froth, which carries with it the greater part of the yeast and other solid matters, what remains of these being got rid of by the workman working his finger round the neck of the bottle, whereby they are detached and forced out by the still rising froth. The wine is now dosed again with liqueur, the bottles filled up, wired, and the neck wrapped with foil ready for shipment.

4. Manufacture of Fortified, Mixed, and Imitation Wines.—All the sweet heavy wines, like sherry, malaga, and port, are characterized by a high alcohol percentage, ranging from sixteen to twenty or twenty-two. This they cannot acquire through fermentation alone, as twelve to thirteen per cent. seems to be the limit of alcohol developed in a wine by direct fermentation. They have the additional alcohol added to them directly in order to give them keeping qualities. With some sweet wines the alcohol is added to the must before the fermentation in order that the fermentation shall be arrested, while a certain amount of sugar remains in the wine unchanged. The quality of wines is often improved by blending. Light wines with too little alcohol are mixed with stronger wines with the formation of an excellent product with better keeping qualities, which can then be transported to long distances without injury. These mixtures can best be made when the wines are new, in order that after mixing they may undergo an insensible fermentation and take a character distinctive of the new product.

The practice of adding flavoring substances totally foreign to the constituents of the must to new and inferior wines in order that they may take the flavor and appearance of older and more valuable wine has also become very wide-spread. Such practices are of course illegal in all countries where laws against adulteration are enforced. Thus, elder flowers, orris-root, iris, cloves, oil of bitter almonds, and numerous perfumes, such as oil of orange flowers, of neroli, of petit-grain, and of violet, are used, as well as coloring infusions like raspberries and walnuts. The heavy wines are the ones most generally imitated. Port is frequently flavored with a mixture of elderberry juice, grape juice, brown sugar, and crude brandy. Sherry often consists of the cheaper Cape wine mixed with honey, bitter almonds, and brandy. In Spain and Southern France a wine prepared from the vine known as the *Teinturier* and possessing an intense bluish-red color is extensively used for coloring of other wines.

In recent years, because of the deficiency in the wine crop of France due to the ravages of the *Phylloxera*, the production of wine from dried raisins or prunes has enormously increased. This product, known as "vin de raisin sec," is said to be a very close imitation of natural French wines. Spon * gives the following as the components of such a raisin wine:

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* Spon's Encyclopedia of Industrial Arts, vol. ii. p. 444.

| | | | |
|---|---|---|---|
| White sugar | 5 kilos. | Common brandy | 12 litres. |
| Raisins | 5 kilos. | River water | 95 litres. |
| Common salt | 125 grammes. | Gall-nuts (bruised) | 20 grammes. |
| Tartaric acid | 200 grammes. | Brewer's yeast (in paste) | 200 grammes. |

To make this wine of a red color it is necessary only to add to the above ingredients two hundred and fifty to three hundred grammes of dry picked hollyhocks, taking care to keep them at the bottom of the cask.

The reports of the United States consular agents show that the manufacture of this raisin wine has become an industry of large proportions in France at the present time. A significant additional indication of the development of this artificial wine industry and of the similar one of petiotizing in France is found in the statement of the amounts of cane-sugar used by French wine manufacturers in recent years. In 1885 there was used in France for the manufacture of grape wines 7,933,887 kilos. of cane-sugar; in 1886, 27,856,592 kilos.; for the manufacture of fruit wines in 1885, 24,142 kilos. of sugar; in 1886, for the same purpose, 145,555 kilos. Most of this fruit wine forms the basis of factitious champagne.

## III. Products.

The normal constituents of a natural wine agree of course with those contained in the must, except in so far as new compounds have been developed by the fermentation process and previously existing ones have been decomposed or made to separate out.

We may divide the constituents of wine into two classes, volatile and fixed. The volatile matters are as follows: Water (eighty to ninety per cent.); alcohol (five to fifteen per cent.); glycerine (two to eight per cent.); volatile acids, acetic, œnanthic, etc., constituting one-fourth to one-third of the total acidity; aldehyde, compound ethers, together with other fragrant indefinite constituents, which give the wine its flavor and bouquet. The fixed matters are glucose, or grape-sugar, in small quantities in most wines; bitartrate of potash, tartaric, malic, and phosphoric acid, partly free and partly combined with various bases, of which compounds phosphate of lime is the most abundant, constituting from twenty to sixty per cent. of the weight of the ash, the remainder being chiefly carbonate of potash, resulting from the calcination of the bitartrate, with a little sulphate and traces of chlorides; coloring matters; pectin and analogous gummy matters; tannin, one to two per cent. in red wines and traces only existing in white wines.

No very simple scheme of classification is possible, as the methods and products of most countries are not fixed by rule, but vary widely according to the season and market. Still, we may distinguish between the red and white, and the sweet and the dry, wines; between the light and delicately-flavored German and French wines and the more fiery but coarser Italian and Swiss wines; between natural wines and those fortified by addition of alcohol, as port, sherry, and madeira; between still wines and effervescing or champagne wines.

Most of these terms have already found their explanation in the description of the processes of manufacture. We may add that a *sweet* wine is one in which a notable portion of the original grape-sugar of the must has escaped fermentation, or to which an addition of sugar has been made subsequent to the main fermentation. A *dry* wine, on the contrary, is one in which the sugar, whether originally present or subsequently added, has

almost all undergone change in the processes of fermentation. *Champagnes* are wines in which a supplementary fermentation is purposely developed subsequent to the bottling, whereby quantities of carbon dioxide gas are developed and held dissolved under pressure. On opening the bottles and thus relieving the pressure a brisk effervescence follows, due to the escape of the absorbed gas. Champagne-makers distinguish three grades of effervescence. In *mousseux* the pressure in the bottle amounts to from four to four and a half atmospheres; in *grand mousseux* it reaches five atmospheres; and less than four atmospheres' pressure constitutes *cremant* (from *la crème*, "cream"), a wine which throws up a froth, but does not give off carbonic acid violently. Some manufacturers also distinguish a grade *demi-mousseux*.

Of natural and unfortified foreign wines the following analyses from Elsner* refer to German wines exclusively:

| | Specific gravity. | Percentage of alcohol. | Percentage of extract. | Percentage of free acid (as tartaric). | Percentage of ash. | Percentage of phosphoric acid. |
|---|---|---|---|---|---|---|
| Rhine wines, Rüdesheimer . . . | 0.9960 | 9.30 | 1.97 | 0.50 | 0.20 | 0.020 |
| " " Rauenthaler . . . . | 0.9960 | 9.25 | 2.10 | 0.54 | 0.19 | 0.023 |
| " " Johannisberger . . | 0.9958 | 8.60 | 2.20 | 0.52 | 0.19 | 0.023 |
| " " Hochheimer . . . . | 0.9935 | 8.00 | 1.50 | 0.72 | 0.16 | . . . |
| " " Niersteiner . . . . | 0.9956 | 7.54 | 1.75 | 0.62 | 0.18 | 0.012 |
| Moselle wines, Brauneberger . . . | . . . | . . | 2.60 | . . | 0.18 | 0.041 |
| " " Pisporter . . . . . | . . . | . . | 2.40 | . . | 0.15 | 0.038 |
| " " Zeltinger . . . . . | . . . | . . | 2.40 | . . | 0.16 | 0.039 |
| Hessian wines, Bodenheimer . . . | 0.9930 | 7.54 | 1.25 | 0.63 | 0.14 | . . . |
| " " Laubenheimer . . | 0.9934 | 6.83 | 1.00 | 0.60 | 0.10 | . . . |
| " " Liebfrauenmilch . | 0.9940 | 8.00 | 1.96 | 0.62 | 0.20 | . . . |
| Palatinate wines, Deidesheimer . | 0.9968 | 9.60 | 2.12 | 0.50 | 0.18 | . . . |
| " " Oppenheimer . | 0.9935 | 8.87 | 1.50 | 0.60 | 0.16 | . . . |
| " " Wachenheimer. | 0.9954 | 8.65 | 1.72 | 0.65 | 0.17 | . . |
| Franconian wines, white . . . . | 0.9943 | 6.65 | 1.20 | 0.60 | . . | 0.015 |
| " " red . . . . . | 0.9932 | 8.00 | 1.50 | 0.47 | 0.20 | . . . |

The following analyses of French wines are from the official report of the Laboratoire Municipal at Paris for 1883:†

| | Alcohol by volume. | Grammes per Litre. | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Extract at 100° C. | Extract in vacuo. | Ash. | Tartar. | Reducing sugar (as glucose). | Sulphate of potash. | Acidity (in $H_2SO_4$). |
| Bordeaux wines, St. Estephe, 1878 . . . . . . . . . | 11.1 | 22.4 | 28.3 | 2.20 | 1.31 | 1.50 | 0.49 | 2.96 |
| " " Medoc, 1880 . . . . . . . . . . | 10.3 | 19.0 | 23.7 | 2.05 | 1.42 | 0.9 | 0.76 | 3.96 |
| " " Latour, 1878 . . . . . . . . . . | 9.5 | 17.0 | 22.8 | 2.14 | 2.07 | 1.1 | 0.50 | 4.06 |
| " " Chateau Margaux, 1878 . . . . . | 10.2 | 23.6 | . . | . . . | . . . | 1.5 | 0.48 | . . |
| " " Larose, 1877 . . . . . . . . . . . | 11.2 | 23.0 | 30.1 | 2.34 | 2.44 | 1.3 | 0.63 | . . |
| " " (white,) Sauterne, 1880 . . . . . | 10.4 | 16.0 | . . | | . . | 3.6 | 0.53 | . . |
| Burgundy wines, Chambertin, 1882 . . . . . . . . | 11.5 | 23.3 | 29.5 | 1.77 | 3.57 | 1.4 | 0.55 | . . |
| " " (white,) Chablis, 1878 . . . . . . | 11.0 | 16.7 | . . | . . | . . | 0.6 | 0.38 | . . |
| Lower Burgundy, average of 7 analyses . . . . . | 7.8 | 20.2 | . . | . . | . . | 1.2 | 0.37 | . . |
| Upper Burgundy, average of 25 analyses . . . . . | 9.1 | 20.7 | . . | . . | . . | 1.1 | 0.48 | . . |

* Praxis des Nahrungsmittels Chemiker, 1880, p. 103.
† Deuxième Rapport du Laboratoire Municipal, Paris, 1884.

Of sweet and fortified or treated wines the following analyses are given by König.*

| | Specific gravity. | Alcohol by weight. | Extract. | Sugar. | Tartaric acid. | Glycerine. | Albuminoids. | Ash. | Phosphoric acid. | Sulphuric acid. |
|---|---|---|---|---|---|---|---|---|---|---|
| Tokay, 1868 | 1.0879 | 9.80 | 26.36 | 22.11 | 0.509 | 0.212 | 0.427 | 0.343 | 0.050 | 0.061 |
| Tokay, Ausbruch, 1866 | 1.0588 | 10.29 | 18.34 | 14.99 | 0.517 | 0.234 | 0.389 | 0.300 | 0.074 | 0.022 |
| Ruster, Ausbruch, 1872 | 1.0849 | 8.96 | 23.64 | 21.74 | 0.512 | 0.162 | 0.231 | 0.409 | 0.057 | 0.035 |
| Malaga, 1872 | 1.0691 | 13.23 | 21.23 | 16.57 | 0.416 | 0.248 | 0.217 | 0.239 | 0.042 | 0.026 |
| Muscat wine, 1872 | 1.0574 | 10.02 | 16.91 | 15.52 | 0.555 | 0.298 | 0.151 | 0.312 | 0.036 | 0.073 |
| Port wine (white), 1860 | 1.0126 | 16.28 | 8.83 | 4.88 | 0.538 | 0.168 | 0.094 | 0.208 | 0.035 | 0.039 |
| Port wine (red), 1865 | 1.0125 | 17.93 | 8.83 | 6.42 | 0.451 | 0.145 | 0.200 | 0.236 | 0.032 | 0.019 |
| Marsala (Ingham) | 0.9966 | 16.73 | 4.94 | 3.48 | 0.396 | 0.298 | 0.150 | 0.270 | 0.024 | 0.087 |
| Marsala (Woodhouse) | 1.0111 | 15.52 | 5.45 | 3.78 | 0.470 | 0.457 | 0.231 | 0.418 | 0.024 | 0.155 |
| Madeira, 1868 | 1.0018 | 15.34 | 5.33 | 3.39 | 0.489 | 0.291 | 0.144 | 0.376 | 0.082 | 0.081 |
| Sherry, 1870 | 0.9952 | 18.66 | 3.78 | 1.88 | 0.438 | 0.506 | 0.200 | 0.483 | 0.032 | 0.184 |
| Sherry, Amontillado, 1870 | 0.9924 | 16.34 | 2.68 | 0.52 | 0.490 | 0.560 | 0.200 | 0.650 | 0.038 | 0.268 |
| Samos wine. 1872 | 1.0519 | 10.97 | 14.46 | 11.82 | 0.502 | ... | 0.237 | 0.563 | 0.058 | 0.044 |

Two analyses of champagne and effervescing wine are also given by König :†

| | Specific gravity. | Alcohol by weight. | Extract. | Sugar. | Tartaric acid. | Glycerine. | Albuminoids. | Ash. | Phosphoric acid. | Sulphuric acid. |
|---|---|---|---|---|---|---|---|---|---|---|
| **Champagne, Carte Blanche** | **1.0433** | **9.51** | **18.96** | **11.53** | **0.581** | **0.084** | **0.219** | **0.184** | **0.027** | **0.017** |
| **Effervescing Rhine wine** | **1.0374** | **9.80** | **10.88** | **8.49** | **0.566** | **0.062** | **0.294** | **0.171** | **0.084** | **0.026** |

Of American wines a large number have been investigated by the United States Bureau of Agriculture. A selection from those analyzed by H. B. Parsons‡ in 1880 is given :

| | Specific gravity. | Alcohol by weight. | Alcohol by volume. | Extract. | Ash. | Glucose. | Total acid as tartaric. | Fixed acids as tartaric. | Volatile acid as acetic. |
|---|---|---|---|---|---|---|---|---|---|
| *Dry red wines:* | | | | | | | | | |
| Concord, Virginia, 1879 | 0.9953 | 8.83 | 11.08 | 2 10 | 0.174 | Trace. | 0.709 | 0.452 | 0.206 |
| Clinton, Virginia, 1879 | 0.9950 | 9.82 | 12.31 | 2.36 | 0.238 | None. | 0.784 | 0.513 | 0.217 |
| Norton's Virginia, 1879 | 0.9937 | 10.21 | 12.77 | 2.88 | 0.298 | Trace. | 0.772 | 0.377 | 0.316 |
| Ives's Seedling, Virginia, 1879 | 0.9944 | 8.68 | 10.82 | 2.18 | 0.247 | Trace. | 0.723 | 0.512 | 0.169 |
| Sonoma Red Mission, California, 1879 | 0.9968 | 7.99 | 10.03 | 2.42 | 0.428 | None. | 0.722 | 0.301 | 0.337 |
| Sonoma Red Zinfandel, California, 1879 | 0.9962 | 7.80 | 9.78 | 2.43 | 0.255 | Trace. | 0.693 | 0.391 | 0.242 |
| Concord Bouquet, New Jersey | 0.9928 | 9.84 | 12.31 | 2.18 | 0.141 | 0.71 | 0.741 | 0.272 | 0.375 |

* Nahrungs- und Genussmittel, vol. ii. p. 463. † Ibid., p. 464.
‡ United States Bureau of Agriculture, Bulletin No. 13, pp. 334–338.

| | Specific gravity. | Alcohol by weight. | Alcohol by volume. | Extract. | Ash. | Glucose. | Total acid as tartaric. | Fixed acids as tartaric. | Volatile acid as acetic. |
|---|---|---|---|---|---|---|---|---|---|
| *Dry white wines:* | | | | | | | | | |
| Brocton Catawba, New York | 0.9890 | 12.28 | 15.30 | 2.09 | 0.121 | ... | 0.542 | 0.470 | 0.068 |
| Missouri Catawba, Missouri | 0.9911 | 8.88 | 11.08 | 1.67 | 0.129 | Trace. | 0.772 | 0.387 | 0.308 |
| Ohio Catawba, Ohio | 0.9892 | 10.25 | 12.77 | 1.63 | 0.118 | Trace. | 0.728 | 0.424 | 0.243 |
| Ruländer, Virginia, 1880 | 0.9914 | 10.46 | 13.05 | 1.90 | 0.199 | Trace. | 0.545 | 0.302 | 0.194 |
| Delaware, Virginia, 1880 | 0.9932 | 9.35 | 11.70 | 1.88 | 0.255 | Trace. | 0.562 | 0.332 | 0.184 |
| Taylor, Virginia, 1880 | 0.9921 | 10.37 | 12.96 | 1.99 | 0.185 | Trace. | 0.732 | 0.317 | 0.332 |
| Herbemont, Virginia, 1880 | 0.9928 | 7.78 | 9.80 | 1.60 | 0.146 | None. | 0.562 | 0.302 | 0.208 |
| Dry Muscat, California | 0.9928 | 9.14 | 11.44 | 1.82 | 0.150 | Trace. | 0.619 | 0.248 | 0.289 |
| White Zinfandel, California | 0.9911 | 9.52 | 11.26 | 1.47 | 0.139 | Trace. | 0.590 | 0.227 | 0.290 |
| Riesling, California | 0.9918 | 9.64 | 12.05 | 1.72 | 0.221 | Trace. | 0.696 | 0.210 | 0.389 |
| Gutedel, California | 0.9920 | 9.36 | 11.70 | 1.58 | 0.196 | Trace. | 0.726 | 0.212 | 0.411 |
| Sonoma Mission, California, 1879 | 0.9935 | 8.30 | 10.38 | 1.67 | 0.193 | Trace. | 0.619 | 0.317 | 0.242 |
| *Sweet wines:* | | | | | | | | | |
| Brocton Port, New York | 1.0508 | 10.00 | 13.24 | 17.04 | 0.139 | 11.80 | 0.828 | 0.600 | 0.182 |
| Speer's Port, New Jersey | 1.0213 | 13.67 | 17.59 | 10.69 | 0.309 | 7.44 | 0.705 | 0.347 | 0.286 |
| Port, Los Angeles, California | 1.0339 | 12.68 | 16.52 | 14.18 | 0.345 | 11.39 | 0.508 | 0.348 | 0.128 |
| New York Sherry | 1.0074 | 13.87 | 17.59 | 6.83 | 0.166 | 4.84 | 0.689 | 0.209 | 0.323 |
| Speer's Sherry, New Jersey | 0.9949 | 17.62 | 22.09 | 4.89 | 0.219 | 3.33 | 0.476 | 0.271 | 0.164 |
| California Sherry | 0.9942 | 13.42 | 16.80 | 3.91 | 0.198 | 2.20 | 0.573 | 0.232 | 0.273 |
| Marsala, California | 1.0052 | 16.06 | 20.33 | 6.42 | 0.428 | 3.53 | 0.626 | 0.418 | 0.166 |
| "Eclipse" Extra Dry Champagne | 1.0174 | 9.26 | 11.87 | 7.78 | 0.149 | 6.51 | 0.885 | 0.295 | 0.472 |
| "Gold Seal" Champagne, New York | 1.0402 | 8.26 | 10.82 | 13.31 | 0.110 | 12.02 | 0.880 | 0.447 | 0.346 |
| Cook's "Imperial" Champagne | 1.0207 | 8.41 | 10.82 | 8.47 | 0.130 | 7.23 | 0.779 | 0.470 | 0.247 |
| Sweet Catawba, Bass Island, Ohio | 1.0338 | 11.68 | 15.21 | 14.49 | 0.152 | 11.00 | 0.595 | 0.296 | 0.239 |
| Sweet Catawba, Brocton, New York | 1.0512 | 10.71 | 14.18 | 16.71 | 0.113 | 15.22 | 0.714 | 0.471 | 0.194 |
| Sweet Catawba, Iowa, 1871 | 1.0101 | 9.89 | 12.58 | 7.23 | 0.211 | 4.01 | 0.668 | 0.318 | 0.280 |
| Sweet Muscatel, California | 1.0245 | 17.33 | 18.58 | 31.34 | 0.371 | 25.37 | 0.753 | 0.421 | 0.266 |
| California Angelica | 1.0440 | 8.96 | 11.79 | 14.41 | 0.196 | 12.48 | 0.489 | 0.310 | 0.143 |
| Brocton Sweet Regina | 1.0515 | 9.71 | 12.87 | 16.52 | 0.101 | 15.31 | 0.628 | 0.465 | 0.130 |
| Sweet Delaware, 1879 | 1.0320 | 8.73 | 11.35 | 12.07 | 0.118 | 10.27 | 0.799 | 0.355 | 0.355 |
| Scuppernong, Sweet, 1878 | 1.0404 | 9.06 | 11.87 | 14.13 | 0.132 | 11.56 | 0.758 | 0.323 | 0.348 |
| Scuppernong, Dry, 1879 | 0.9948 | 10.72 | 13.43 | 3.39 | 0.108 | 1.31 | 0.925 | 0.346 | 0.463 |

*Side-products.*—The first of these is the *marc* of the grapes, separated from the must in the original pressing of the grapes, or left when the fermenting must is drained from it. This consists of the stems, skins, and stones of the grapes. If the marc instead of being washed out with water has been merely pressed, it still contains sufficient must to allow of its being used in the manufacture of petiotized wine. Besides this, the marc serves for a great variety of purposes. It is fermented for brandy; it is used with sheet-copper in the manufacture of verdigris; it is used to start the fermentation in vinegar-making; as cattle-food; when dried, as fuel or for fertilizing purposes; the tannic acid is extracted, or it is used direct in producing black colors, and for other minor applications.

The second and more valuable side-product is the deposit formed on the bottom and sides of the casks in which the fermentation takes place. That on the bottom of the casks is called "lees." It contains from thirty to forty per cent. of vegetable matter (from the yeast-cells depositing), the remainder being tartrates, sulphates, (in plastered wines), alumina, phosphoric acid, etc. Its composition is greatly altered by "plastering" the wine, in which case the tartrate exists chiefly as the neutral calcium tartrate instead of the acid potassium salt. The crystalline crust that forms on the sides of the vessels used for fermentation is called "argol," or crude tartar. It varies somewhat in composition, the tartaric acid ranging from forty to seventy per cent. and being always present, chiefly as the acid potassium tartrate. From this crude tartar is prepared, by extraction with boiling water, filtering, and crystallizing, "cream of tartar." This, however, still

contains some calcium tartrate mixed with the acid potassium salt, the amount ranging from two to nine per cent.

## IV. Analytical Tests and Methods.

In 1884 the Imperial German Health Office appointed a commission of experts to report upon the best uniform methods for the analysis of wines. The methods agreed upon by that commission are very generally adopted now in Germany, and largely used elsewhere in guiding wine analysts. These official methods have been fully described and explained in a little work entitled "Weinanalyse," by Dr. Max Barth, Leipzig, 1884.

The *specific gravity* of the wine is determined either by the pyknometer (specific gravity bottle) or by the Westphal balance (see p. 80), the readings of which have been compared with those of the specific gravity bottle. In the case of champagnes and effervescing wines, as was the case with beer, the carbonic acid must be got rid of as far as possible before taking the specific gravity readings.

The *alcohol* is determined by the direct distillation, as described on p. 200. Wines that have a tendency to foam have a little tannin (.1 gramme) added. If one hundred cubic centimetres of the sample is taken, sixty cubic centimetres only need be collected, and will contain all the alcohol. This is then diluted to nearly one hundred cubic centimetres, cooled, uniformly mixed, and then brought exactly to the 100-cubic-centimetre mark, mixed again, and the specific gravity taken. The form of apparatus best adapted for this determination of alcoholic strength of wines and liquors is shown in Fig. 64. For the rapid determination of the alcoholic strength of wines various forms of apparatus have been devised, such as the vaporimeter of Geissler, in which the vapor-tension of an alcoholic liquid exerted upon a column of mercury is made to indicate its percentage strength in alcohol, the ebullioscope of Tabarie, of Malligand and Vidal, and of Amagat, which depend upon the observation of the boiling-points of a spirituous liquor as determining the amount of alcohol contained. None of these can be said to have scientific accuracy,
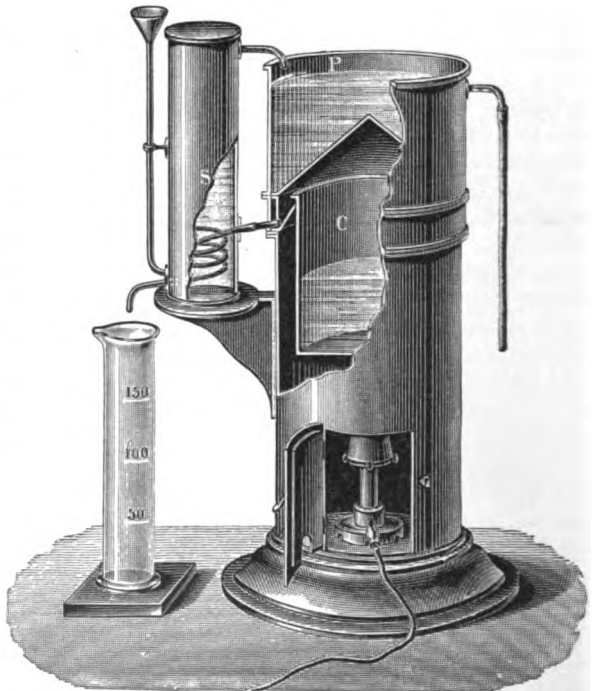
Fig. 64.

as wine is not merely a mixture of alcohol and water, but contains other constituents which affect the results in either case.

The *extract* determination. Here the direct weighing of the residue after evaporation is preferred to the indirect method, fifty cubic centimetres of the wine, measured at 15° C., are to be evaporated on the water-bath in a platinum dish (according to the German wine commission, this dish should be eighty-five millimetres in diameter, twenty millimetres in height, seventy-five cubic centimetres in capacity, and should weigh about twenty grammes), and the residue dried for two and a half hours in a double-walled water drying oven. In the case of wines containing more than .5 per cent. sugar, a smaller quantity must be taken and suitably diluted, so that the extract shall not weigh more than 1.0 to 1.5 grammes. In this method, the loss of glycerine by evaporation is trifling. The indirect method for determining the extract is very like that described under beer (see p. 200) as O'Sullivan's method, except that with wine we divide the excess of specific gravity observed over 1000 by 4.6 instead of 3.86, as the solids of wine have a higher solution density than those of extract of malt. Or with the specific gravity of the de-alcoholized liquid we may get the extract percentage from Hager's tables, which are analogous to those of Schultze for malt extracts before referred to.

The *ash* percentage can be obtained by incineration of the evaporated extract above referred to.

To determine the percentage of *glycerine*, one hundred cubic centimetres of the wine are evaporated down to about ten cubic centimetres in a spacious porcelain dish; some sand and milk of lime are then added till the reaction is strongly alkaline and the mixture evaporated almost to dryness. The residue is next treated with fifty centimetres of ninety-six per cent. alcohol, warmed and stirred on the water-bath, and the solution obtained then passed through a filter. The insoluble matter is washed with successive small portions of hot alcohol (ninety-six per cent.), of which fifty to one hundred and fifty cubic centimetres will as a rule suffice, so that the entire filtrate will be from one hundred cubic centimetres to two hundred cubic centimetres. The alcoholic extract is now evaporated to a viscous consistency, and the residue taken up with ten cubic centimetres of absolute alcohol; this solution is mixed with fifteen cubic centimetres of ether in a stoppered flask and the mixture allowed to stand until clear. The clear liquid is decanted or filtered into a light tared glass vessel, carefully evaporated, and the residue dried for one hour in the water-bath. It is then cooled and weighed. In the case of sweet wines (containing more than five per cent. of sugar), only fifty cubic centimetres of the wine are taken for the estimation of the glycerine; sand and lime are added, and the mixture is warmed on the water-bath. After cooling it is treated with one hundred cubic centimetres of ninety-six per cent. alcohol, the precipitate formed allowed to settle, the solution filtered, the insoluble matter washed with spirit, and the alcoholic filtrate treated as above described.

To estimate the *sugar* in wine, Fehling's solution is used, as the sugar should be only glucose. After neutralization of the wine with sodium carbonate, the determination is made (using the separately preserved solutions for Fehling's mixture. See p. 159). Strongly-colored wines must be first decolorized. If the sugar percentage is low, it is done with purified bone-black; if they contain over .5 per cent. of sugar, bone-black cannot be used because of its absorptive power, and basic acetate of lead must be substi-

tuted. After filtering, the wine is then treated with sodium carbonate and Fehling's solution. If the polarization indicates the presence of cane-sugar, the solution must be inverted (see p. 158) and then the Fehling's test applied again, and the cane-sugar calculated from the difference in the two readings. The Fehling's test is best carried out gravimetrically, and from the weight of reduced copper the corresponding amount of glucose can be obtained from the tables.

The *polarization*, which is essential in the case of heavy wines to indicate the nature of the sugar contained, is carried out as follows: *With white wines*, to sixty cubic centimetres of the wine are added three cubic centimetres of the basic acetate of lead solution and the precipitate filtered off on a dry filter. To 31.5 of the filtrate is added 1.5 cubic centimetres of a saturated solution of sodium carbonate and the solution again filtered and the polarization tube filled with the filtrate. The dilution of the original wine in this case is 10 : 11. *With red wines*, sixty cubic centimetres of the wine are treated with six cubic centimetres of the lead solution, and to thirty-three cubic centimetres of the filtrate three cubic centimetres of the saturated sodium carbonate solution added, the solution filtered and polarized. The dilution here is 5 : 6. This diluted solution is observed in the 220-millimetre tube of the polariscope, and large and accurate instruments are necessary.

The *free acids* (total acid-reacting constituents of the wine) are estimated in ten to twenty cubic centimetres of the wine by means of one-third or one-tenth normal alkali. Any considerable quantity of carbonic acid to be first removed by shaking. The "free acids" to be calculated into and given as tartaric acid ($C_4H_6O_6$).

The *volatile acids* are determined by steam distillation and calculated as acetic acid ($C_2H_4O_2$).

The quantity of *non-volatile acids* calculated as tartaric is found by subtracting the equivalent of the acetic acid in tartaric acid from the *free acids* previously determined.

These three determinations are all that are usually made in wine analyses. If a special qualitative test for free tartaric acid is desired or, in case it be shown to be present in appreciable quantity, a quantitative method for its determination, they can be made by Nessler's method, for details of which the reader is referred to Barth's "Weinanalyse" before mentioned, or to a summary of its methods in the "Journal of the Society of Chemical Industry," 1885, p. 553.

The *tannin* may be determined by Neubauer's method with permanganate of potash, or approximately by the following procedure: the free acids in ten cubic centimetres of the wine are neutralized with standard alkali, after which one cubic centimetre of a forty per cent. solution of sodium acetate is added, and finally a ten per cent. solution of ferric chloride, drop by drop, and avoiding excess. One drop of this solution suffices for the precipitation of every .05 per cent. of tannin.

*Salicylic Acid.*—To detect this acid, one hundred cubic centimetres of the wine are shaken repeatedly with chloroform, the latter is evaporated, and the aqueous solution of the residue tested with very dilute ferric chloride solution. For the purpose of an approximate quantitative estimation, it is sufficient, on the evaporation of the chloroform, to once recrystallize the residue from chloroform and weigh it.

One of the most important questions that arises in the examination of

red wines is as to the genuineness of the *coloring matter*, as both vegetable and artificial dye colors have been used for years to imitate the natural coloring matter in the manufacture of factitious red wines. Very elaborate schemes for the recognition of foreign coloring matters, including both the vegetable coloring matters like dye-woods and color-yielding berries and the large number of the newer coal-tar colors, have been given by Gautier * and by Chas. Girard,† the director of the Laboratoire Municipal in Paris, to which we can only give references. The coloring matters most generally used to imitate the natural pigment of the grape-skins are fuchsine, cochineal, alderberry, hollyhock, and logwood. Dupré tests the coloring matter as follows: Cubes of jelly are prepared by dissolving one part of gelatine in twenty parts of hot water and pouring the solution in moulds to set. These are immersed in the wine under examination for twenty-four hours, then removed, slightly washed, and examined. Pure wine will color the gelatine only very superficially; the majority of other coloring matters (fuchsine, cochineal, logwood, Brazil-wood, litmus, and indigo) penetrate more readily, passing to the very centre of the cube. A confirmative test can also be made with the dialyzer. The coloring principle of pure wine when subjected to dialysis does not pass through the animal membrane to any decided extent, while the color of logwood, Brazil-wood, and cochineal easily dialyzes. If rosaniline colors alone are to be tested for, the procedure of Falière as improved by Nessler and Barth can be followed. One hundred cubic centimetres of the wine are shaken in a stoppered jar with thirty cubic centimetres of ether and five cubic centimetres of strong ammonia, and then twenty cubic centimetres of the ethereal layer removed with a pipette and evaporated in a capsule containing a thread of white wool five centimetres in length. Similar threads are dyed with known quantities of magenta, and from a comparison of tints the amount of the added coloring matter in the wines is inferred. This test will detect minute quantities of fuchsine or aniline red. If the same test be carried out without adding ammonia, the acid rosaniline colors and similar dyes will be extracted. The fact that pure wine color is not changed or decolorized by nascent hydrogen (zinc and acid), while most of the aniline dyes are decomposed by it, is also used as a test.

## *D.* MANUFACTURE OF DISTILLED LIQUORS, OR ARDENT SPIRITS.

This industry differs radically from the two fermentation industries already described, firstly, in that the effort is made to push the fermentation to the fullest possible limit, so that the maximum quantity of alcohol may be produced, and, secondly, in that this product of fermentation is then distilled, and it may be redistilled in order to get a distillate richer in alcohol than the fermentation product itself can be. The end to be attained may be either the production of an alcoholic beverage as the product of distillation or of raw spirit, which takes name from the material used, as "grain spirit," "potato spirit," "corn spirit," etc. From this raw spirit by the processes of rectification are obtained the "rectified spirit" used as the basis of the manufacture of various alcoholic beverages and as a solvent in various manufacturing processes, and by purification and dehydration the absolute ethyl alcohol of the chemist.

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* Wynter Blyth, Foods, Composition and Analysis, p. 464.

† Deuxième Rapport du Laboratoire Municipal.

## I. Raw Materials.

These may be divided into three classes: First, alcoholic liquids, themselves the product of fermentation,—these require only to be submitted to distillation in order to yield the stronger spirit; second, solid and liquid materials containing some variety of sugar, whether cane-sugar, grape-sugar, or maltose, which are directly or indirectly fermentable; and, third, starch-containing cereals and all materials capable under the influence of diastase or dilute acids of hydrolysis and the production of a fermentable sugar.

1. ALCOHOLIC LIQUIDS (*Wines*).—The distillation of wines is followed for the production of an alcoholic beverage (brandy) which takes to some degree its flavor and bouquet from the wines used in the distillation. While factitious brandies are largely made from grain or potato spirit, the true product from wine is always regarded as superior.

The manufacture of wine brandy has been chiefly carried out in France, and in minor degree in Spain and Portugal. Within recent years California wines have also been used for the manufacture of brandies. The French wines which are used are largely those of the departments Charente and Charente-Inférieure, in the southwest of France, and the product is all known as Cognac brandy.

White wines are said to yield a superior spirit to that obtained from red wines, and older wines better than newer ones. About eight and a half hectolitres of wine are needed to produce one hectolitre of brandy. Because of the ravages of the Phylloxera insect, the manufacture of genuine wine Cognac has decreased enormously in France in recent years, while the manufacture of factitious Cognac has correspondingly increased. Thus we find it officially stated * that the production of alcohol from wine in France had decreased from 530,000 hectolitres in 1875 to 14,678 hectolitres in 1883.

The marc of the grapes, as already stated (see p. 211), is also utilized in the manufacture of an inferior grade of brandy, known in France as *eau de vie de marc*. The lees, or sediment, of the wine-casks are also used in this same way. This brandy is not necessarily sold for consumption, but is used to strengthen the alcoholic percentage of wines in which fermentation is to be arrested.

2. SUGAR-CONTAINING RAW MATERIALS.—The most important sugar-yielding materials cultivated on a large scale, it will be remembered, are the sugar-cane and the sugar-beet. The sugar-canes are not used directly for the production of spirits (except in the case of accidental souring), and the "bagasse," although still containing saccharine juice, is too bulky, and hence is at once burned as fuel, but the molasses obtained on so large a scale in the extraction of raw sugar is a most valuable material for the purpose. Throughout both the West Indies and the East Indies enormous quantities of this molasses are fermented and the resultant product distilled for rum. Even the sugar-scums obtained in the defecating and concentrating of the sugar juice are fermented, and produce an inferior grade of rum.

With the sugar-beet, both the beet itself and the beet-molasses are utilized, the former being used in France and the latter in both France and Germany. Sweet fruits, the juice of which is rich in sugar, also serve as raw materials for the spirit industry. Thus peaches, plums, and cherries

* Deuxième Rapport du Laboratoire Municipal, p. 272.

are much used in different countries for the manufacture of fruit brandy, and the fermented juice of the date-palm in the East Indies and of the plantain in the West Indies both serve for the distillation of an alcoholic beverage.

3. STARCH-CONTAINING RAW MATERIALS.—This list includes the main sources for the distillation of spirits, as the high percentage of starch in many cereals, ranging from sixty to seventy-seven per cent., the ease with which the starch can be converted into fermentable sugar under the influence of diastase or dilute acids, and the cheapness of these starchy products of nature all combine to make them for most countries the cheapest and best materials for the spirit industry. In the United States, the three cereals used almost exclusively for the manufacture of distilled liquors are corn, rye, and malted barley; in England, barley, both raw and malted, rye, corn, and rice; in Germany the potato is almost the only starchy material used. The composition of the several cereals showing their relative percentage of starch was given on p. 169.

## II. Processes of Manufacture.

1. PREPARATION OF THE WORT.—In England and the United States, where grain spirit is mainly manufactured, the first process is that of saccharifying the starch of the grain. In the special cases where malted grain alone is used, the mash process somewhat resembles that already described under beer-brewing. Most distillers, however, use mixtures of raw and malted grain, in which the raw largely predominates, being often ten to one or even more, as a very small quantity of diastase can be made to convert a large amount of starch into maltose or fermentable sugar. It is stated, moreover, that the yield of spirit is larger when several kinds of grain are mixed than when one kind is used singly. The mixture of raw and malted grain, properly ground, is put into the mash-tub (see Fig. 62, p. 193) with water at 150° F. and agitated. This first mashing requires from one to four hours, the larger the quantity of raw grain used the longer being the time required for mashing. The temperature of the mixture is kept up to about 145° F. by the successive additions of water at a somewhat higher temperature (190° to 200° F.). The object of the distiller in this is somewhat different from that of the beer-brewer. He wishes to convert the whole of the starch, if possible, into maltose, which is directly fermentable by the action of yeast, while the dextrine is not, so he must mash at not much over 146°, which it will be seen from Fig. 61 (p. 187) is the limit above which the maltose production begins to decrease. When the gelatinization of the starch is complete, the temperature of the mash may go slightly higher. By keeping within this limit of temperature, a minimum of diastase from the small admixture of malt will gradually change not only the starch, but bring about a hydration of the residual dextrine, converting it into maltose. When the wort has acquired its maximum density, as found by the saccharometer, it is drawn off, and fresh water at about 190° F. is run upon the residue in the mash-tub and allowed to infuse with it for one or two hours. This second wort is then added to the first. A third weak wort is often obtained, and used to infuse new lots of grain. The mash is then cooled down promptly to the temperature required for fermentation so that the acetous fermentation may not set in.

It is stated that in this method of direct mashing ten per cent. of the

starch escapes decomposition, even although the grain may be taken finely ground. Hence a preliminary warming with water to which a little green malt is sometimes added, followed by heating with water under a pressure of several atmospheres, now often precedes the addition of the main quantity of the malt, which is to complete the conversion of the starch and dextrine into maltose. In this way the loss may be reduced from ten to five per cent.

In Germany potatoes constitute the chief raw material for the spirit manufacture. They contain from eighteen to twenty per cent. of starch only, however, while the cereals contain over sixty per cent. The amount of the malt needed for the saccharification of the starch can therefore be correspondingly reduced. Instead of mashing the ground, rasped, or chipped potatoes in open mash-tubs as was formerly done, they are now first steamed under a pressure of two to three atmospheres, whereby the starch-containing cells are thoroughly ruptured and the starch put in condition to be easily acted upon by the diastase. Among the forms of apparatus based upon this principle may be mentioned those of Hollefreund, Bohm, Henze, and Ellenberger. In that of Henze, which has been largely adopted, the potatoes, after steaming under a pressure of several atmospheres, are so disintegrated that on opening a valve in the bottom of the vessel the pulp is forced out through a grating in a thin stream. This is cooled, mixed with the requisite quantity of malt, and started to mashing. In the Hollefreund and in the Bohm apparatus, the steaming, disintegrating, and mashing all take place in the same closed vessel, the malt being added after the disintegrated mass has been properly cooled down. Green malt is found to work better in this case than air malt, and produces more alcohol.

2. Fermentation of the Wort, or Saccharine Liquid.—In the case of mashing, as described above, either with grain or with potatoes, the wort must first be cooled down before adding the yeast and starting the fermentation. The yeast used is a surface yeast, and either fresh brewer's yeast or compressed yeast (previously softened in warm water) may be used. The procedure is now somewhat different, according as we have a grain-mash or a potato-mash to deal with. In the former case, using a thin wort drained from the exhausted grain, it has been found that the best results are obtained when the temperature during fermentation rises to about 33° or 34° C. (92° to 94° F.), as shown in Fig. 61 (see p. 187); in the latter case, where the entire mash, solid matter and all, is fermented, the fermentation begins at a much lower temperature, and the heat evolved in the fermentation of such a concentrated wort ultimately carries the temperature to the same maximum. In the English plan, considerable lactic acid forms because of the higher temperature, and this is, of course, at the expense of the alcohol formation, while in the German plan, because of the low initial temperature of the fermentation, comparatively little lactic acid is produced, and when the higher temperatures are reached the mixture already contains so much alcohol that the lactic acid ferment grows with considerable difficulty.

For one thousand litres of grain-mash, eight to ten litres of brewer's yeast or one-half kilo. of compressed yeast are used; for one hundred litres of potato-mash, one to two litres of brewer's yeast or three-fourths to one kilo. of compressed yeast are needed.

The fermentation is sometime divided into several stages: the *preliminary* fermentation, in which the yeast-cells grow without much alcohol formation; the *main* fermentation, in which the maltose is fermented; and

the *after*-fermentation, in which the dextrine is gradually changed into maltose and this into alcohol.

The time of fermentation varies from three to nine days, but it is carried on until the density of the liquid ceases to lessen or attenuate, which is determined by the saccharometer.

*The coefficient of purity* of a fermentation is a term used to designate what percentage of the available starchy material in a substance has actually undergone the pure alcoholic fermentation. Thus, the reaction $C_6H_{10}O_5 + H_2O = 2C_2H_6O + 2CO_2$ demands from one kilogramme of starch a percentage of alcohol equal to 71.7 litres, and such a yield from one kilogramme of fermented material would indicate a purity coefficient of one hundred per cent. A percentage yield equal to sixty litres of alcohol from one kilo. of material would give a purity coefficient of 83.7 per cent.

The use of hydrofluoric acid or ammonium fluoride, first proposed by Effront as an antiseptic and indirect aid to the alcoholic fermentation, has become quite important in the spirit industry. The advantages claimed for its use are: first, by preventing the losses due to secondary fermentation, the alcohol yield is increased; second, this yield is especially maintained when raw materials of somewhat inferior quality are used, when without the hydrofluoric acid the yield would be diminished; third, the development of foaming in the fermentation is in large degree prevented.

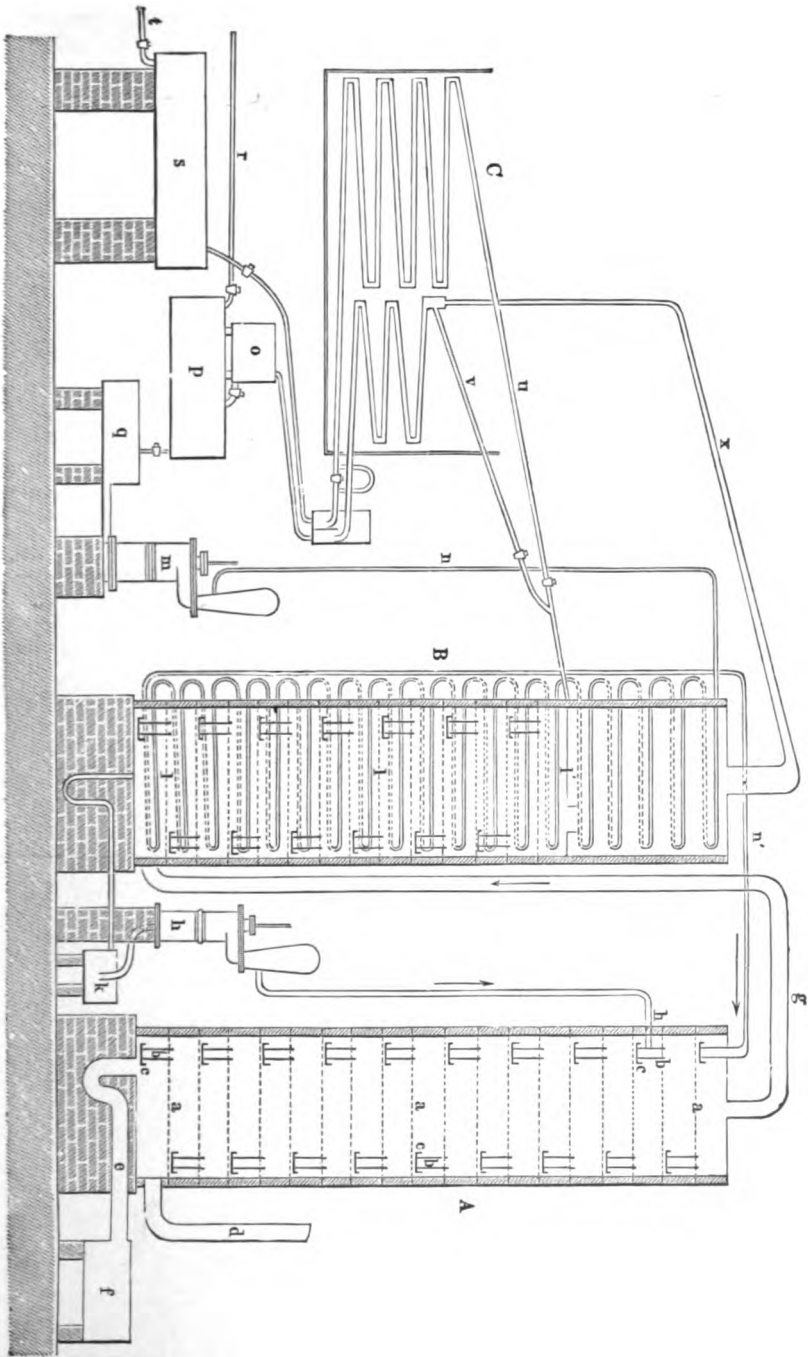
In France, the juice from inferior beets instead of being worked for the extraction of sugar is often fermented and distilled. The juice is made slightly acid with sulphuric acid to prevent any viscous fermentation, and a small quantity of brewer's yeast is added. The temperature of the fermentation is from 20° to 22° C., and the process is usually complete in from twenty-four to thirty-six hours.

The use of the molasses obtained in the extraction of the raw sugar, whether from the sugar-beet or the sugar-cane, is, however, much more common. In France and Germany, where the beet-sugar molasses is produced in large quantities, the molasses originally marking 40° to 48° Beaumé is diluted to 8° or 10° Beaumé, and sulphuric acid of 66° is added to the amount of 1.5 per cent. of the molasses taken. This neutralizes the bases of the beet-molasses and inverts the cane-sugar present, bringing it into fermentable form. Brewer's yeast is then added, and the fermentation proceeds rapidly. The temperature ranges from 22° C., that usually chosen in France, where more dilute solutions are fermented, to 25° to 30° C. in Germany, where the concentration is usually as much as 12° B. Two hundredweight of molasses at 42° B. will furnish about six gallons of pure spirit.

In the West Indies, notably in Jamaica, the cane-sugar molasses is similarly utilized, but the procedure is somewhat different. In this case the addition of yeast is unnecessary, as the nitrogenous matters present suffice to start spontaneous fermentation. The best rum is that gotten from the molasses alone; a second grade is obtained from the skimmings and "sweet-waters" which accumulate in the extraction of the sugar. To these is added some "dunder" (fermented wash, deprived by distillation of its alcohol and much concentrated by boiling), which acts as the ferment and starts the action. Molasses is then added in the proportion of six gallons to every hundred gallons of the fermenting liquid and the action allowed to go to completion. One hundred gallons of this mixture when distilled should yield twenty-five gallons of "low wines" or one gallon of proof rum for each gallon of molasses employed.

3. Distillation of the Fermented Mash, or Alcoholic Liquid.—Upon the construction of apparatus for the distilling from the fermented mash of the alcohol which it contains much skill and ingenuity have been displayed, and some of the later forms of stills and rectifying apparatus employed in large distilleries are wonderfully adapted for obtaining in a continuous operation the purest and strongest alcohol from the crude fermentation products. We may distinguish some five main classes of distilling apparatus, of which the minor varieties are too numerous to be specially enumerated. These classes are: first, simple stills with worm condenser heated by direct firing; second, simple stills with closed "wash-warmer"; third, stills with rectifying "wash-warmer"; fourth, stills with "wash-warmer," rectifying and dephlegmator apparatus for intermittent working; and, fifth, similar forms of construction for continuous working. The first and simplest of these classes hardly needs any special description. The stills are usually of copper, flat-bottomed, and often of great size, especially in Irish and Scotch whiskey distilleries. It is obvious that their use involves a great waste of fuel. Therefore one of the earliest devices for economizing the heat of distillation consisted in interposing between the still and the refrigerating apparatus a "wash-warmer," or vessel filled with the liquid ready for distillation. Through this vessel the pipe conveying the hot vapors to the refrigerator coil passed, and the vapors partly condensing there heated up the wash, which then went into the still quite hot. Dorn's apparatus, still somewhat used in smaller establishments in Germany, accomplished the same thing, and effected a partial rectification of the distillate by having interposed between the still and the refrigerator a vessel divided horizontally into two compartments by a diaphragm of copper. The upper and larger compartment served as a wash-warmer, and through it the tube conveying the vapors from the still passed into the lower compartment, where at first the distillate condensed. As the wash becomes warmed up this distillate gives off alcoholic vapors, which then pass on and are condensed in the worm, while the watery portion is allowed to flow back into the still by a side-connection. It is obvious that this rectifying action can be increased by the introduction of two or more such vessels between the still and the final condenser, and so a distillate much richer in alcohol be obtained.

Another principle was now brought into play in effecting a fractional condensation, that of dephlegmation, or chilling the vapor coming off by contact with metallic diaphragms so that a portion of it, and of course the most watery, is condensed and separated while the richly alcoholic vapor passes on into the rectifier or condenser. Three types of these most elaborate apparatus may be briefly referred to: the Pistorius apparatus, used in Germany for the thick potato-mashes of that country, which is intermittent, the Coffey still, used in England and Scotland for the thinner worts from grain, and the column apparatus, first introduced by Savalle and improved by later inventors, which is used in France for distilling wines and in Germany to follow up the work of the Pistorius or similar apparatus. Both the Coffey still and the column apparatus are continuous in action. In the Pistorius apparatus, two boilers and a wash-warmer are used for the fresh mash, and are connected so that the vapors from the first boiler pass into the second boiler, heating it up and in time driving vapor from it, which then passes around the wash-warmer and goes through several dephlegmators placed one above the other. In these the watery alcohol is continually being condensed and running back to the second boiler, while the uncon-

FIG. 65.

densed vapor which escapes from the top dephlegmator goes finally to the refrigerating apparatus. The Pistorius apparatus has been improved upon by Gall, Schwartz, and Siemens. The Coffey still, illustrated in Fig. 65, consists of two columns placed side by side, made of wood and lined with copper. The analyzer, *A*, is divided into twelve small compartments by four horizontal plates of copper, *a*, perforated with numerous holes and furnished with valves opening upwards. Dropping-pipes, *b b*, are also attached to each plate, the upper end of the pipe being an inch or two above the plate and the lower end dipping into a shallow pan, *c*, placed on the lower plate. The second column or rectifier, *B*, receives the spirituous vapors passing from the column *A* through the pipe *g*. This column is also divided into compartments like *A*, but there are fifteen instead of twelve. The ten lower diaphragms, *l*, are pierced with small holes and furnished with drop-pipes, while the upper five have only one large opening surrounded by a ring to prevent the finished spirit from returning. Between each of these compartments passes a bend of a long zigzag pipe, *n n'*, one end of which is attached to the pump *m*, whilst the other end discharges the contents of the pipe into the top of the column *A*, as indicated by the arrow. The following is the working of the apparatus. In the first place, the fermented liquor or wash is pumped up by the pump *m* until the zigzag pipe is filled and the wort flows over the compartments *a a a*. Steam is then admitted into the compartments of the analyzer by the pipe *d* and heats the wash, which is deprived of all its alcohol by the time it reaches the bottom of the cylinder and flows off by *e f* as spent wash. The strong spirituous vapor passes through *g* to the rectifier, and at last through the worm *c* of the refrigerator into the receiver. The Coffey still is recognized as the best and most economical device for preparing a highly-concentrated spirit in a single operation. It is specially adapted for preparing from grain-mashes what is called "silent spirit," which is almost entirely destitute of flavor, and of a strength ranging from fifty-five to seventy over proof. It is not so well adapted for the distillation of malt whiskey as fire-heated stills, because the peculiar flavor of the whiskey depends upon the retention by the alcoholic distillate of the volatile oils produced in the mash, and the Coffey still separates the alcohol from these as well as other impurities. The forms of apparatus used in France for the distillation of wines are illustrated in that of Cellier-Blumenthal as improved by Derosne, shown in Fig. 66. The alcoholic vapors from *A* pass into *B*, and thence into the rectifying column *C*, which contains a series of perforated metal cups over which wine from the wine-warmer, *E*, is trickling. The vapors thus enriched go rough the upper rectifying column, *D*, and thence to the wine-warmer, *E*, ich serves as a first condenser, and then to the cold condenser, *F*, and so he collecting vessel. After the operation is well under way the supply wine can be introduced from *H* through *G*, *k*, and *E*, while the de-alcoolized liquid can be run off from the lower side of *A*.

Another form of still very largely used in France and Belgium, especially for thin mashes like molasses and beet-mash, is that of Savalle, illustrated in Fig. 67. It is a continuous-working apparatus. *B* is the still proper heated by steam-pipes, *A* is the rectifying column, *C* is for catching froth, *D* is a warm tube condenser and *E* the cold condenser. The elements which form the condensing and rectifying parts of the column *A* are shown in Figs. 68 and 69. The vapors rising pass through the holes of the per- plates, on which rests a layer of condensed liquid which can only

drain down through *d* into the cup *c* placed below it. From these cups it overflows upon the perforated plate and is again drained off by the next connecting tube, *d*. The rising vapors are therefore washed by the liquid upon each perforated plate.

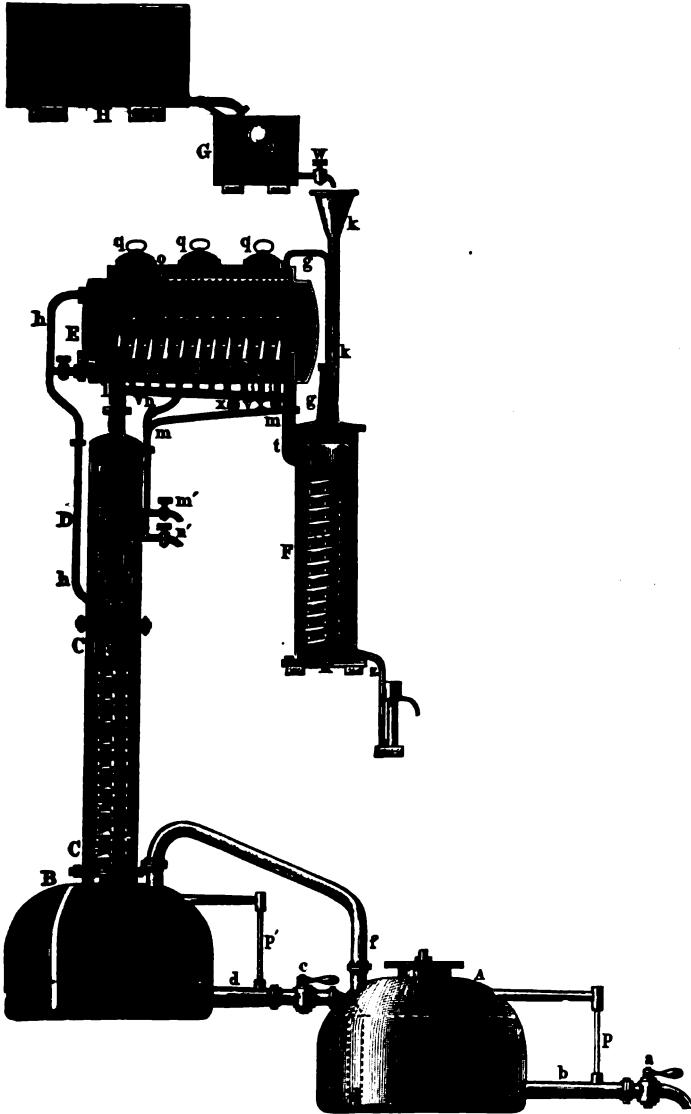
Fig. 66.

4. Rectifying and Purifying of the Distilled Spirit.—The products from the preliminary distillation from the fermented grain- or potato-mash are not at first sufficiently strong, but must be strengthened by rectifying. In England, the spirits obtained by the first distillation from grain-mash are generally called *low wines*, and have a specific gravity of

Fig. 67.

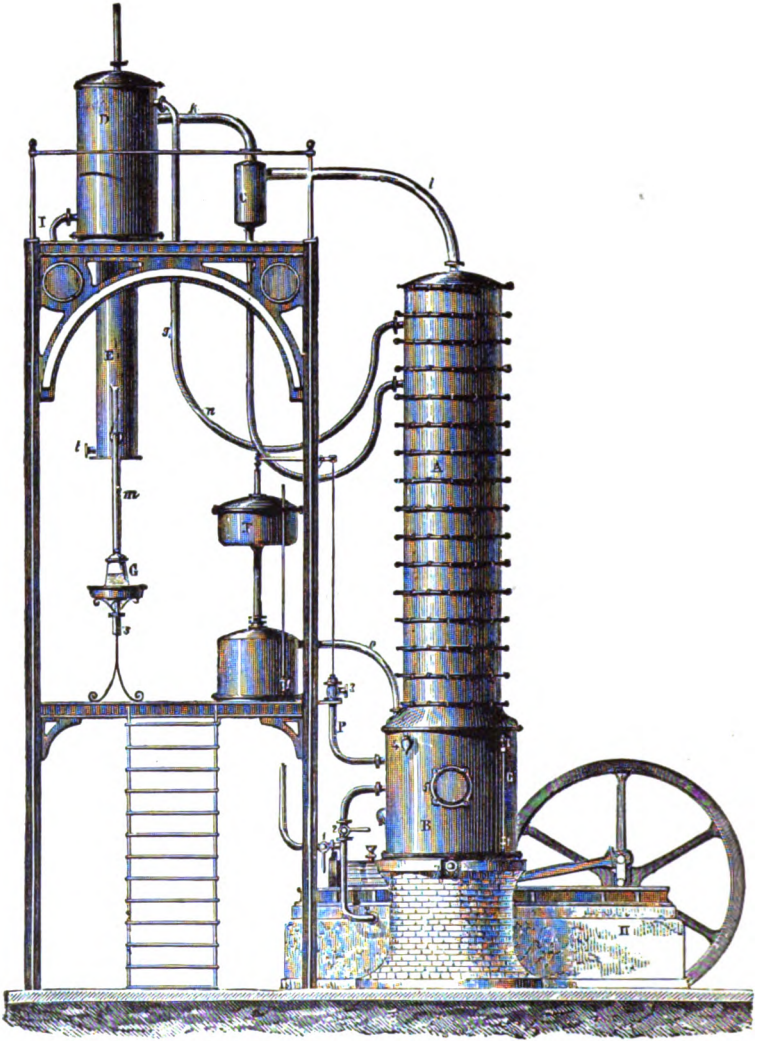



Fig. 68.

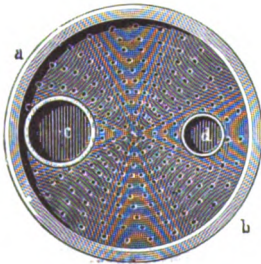



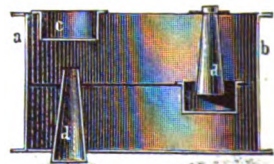
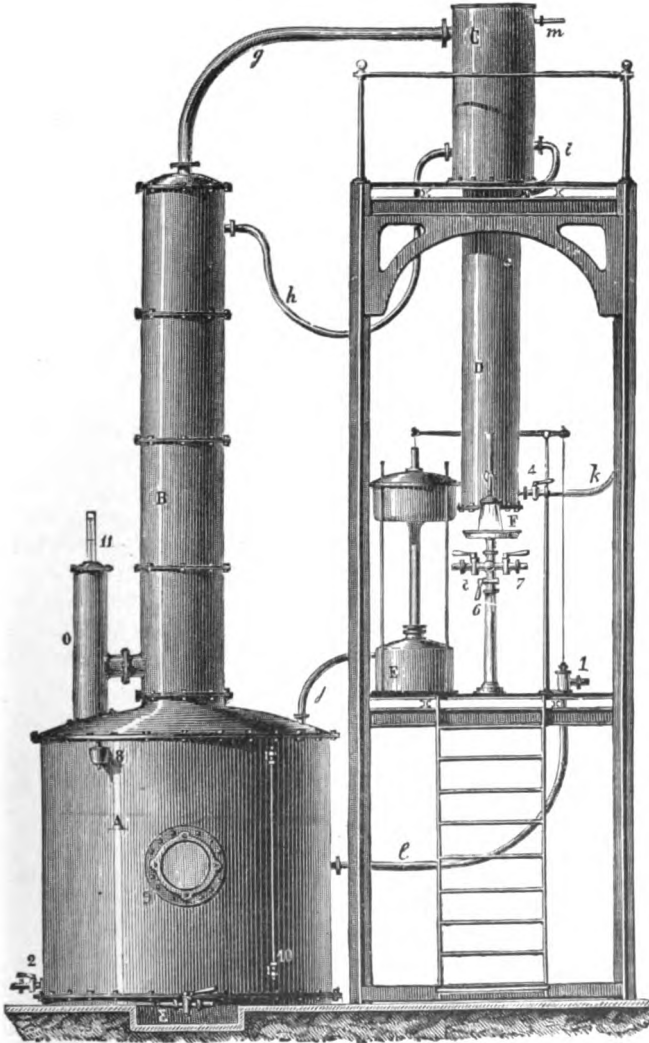
Fig. 69.

about .975. By rectifying, or *doubling*, a crude milky spirit, abounding in oil, at first comes over, followed by clear spirit, which is then caught separately. When the alcoholic strength of the distilled liquid has considerably diminished, the remaining weak spirit that distils over, called *faints*, is caught separately and mixed with the low wines preparatory to another

FIG. 70.

distillation. The rectifying is most rapidly and effectually done in the several forms of column apparatus, the best of which will yield a very pure alcohol in one or two operations.

An improved Savalle rectifying column as used generally in French and Belgian distilleries is shown in Fig. 70. It consists of a still, *A*, neated by closed steam-coils, a rectifying column, *B*, two tubular condensers, *C* and *D*,

from the upper of which any condensed vapors flow back into the rectifying column as "low wines," while the lower condenser takes the more volatile product and passes it on as high-grade alcohol to the receiving-vessel, *F*.

The purifying of raw spirit, notably that from grain and potatoes, from what is called fusel oil (propyl, isobutyl, and amyl alcohols) is also a matter of great importance if the spirit is to be used as the basis of any manufactured liquors. This fusel oil sticks persistently to the alcoholic distillates, and alcohol rectified until it reaches a strength of ninety-five or ninety-six per cent. by volume contains fusel oil. Some acetaldehyde also remains dissolved in the alcohol, giving the raw spirit a bitter taste. Various remedies have been proposed of a chemical nature, such as a treatment of the raw spirit with oxidizing agents like chromic acid and ozone, but they have accomplished little as yet. The method most generally in use is to dilute the alcohol with water until it is about fifty per cent. strength, by which means the fusel oil separates out insoluble in the dilute spirit, and then to filter through wood charcoal. This process seems to be quite successful in removing the higher alcohols. The wood charcoal can be revivified by heating to redness in closed retorts. Another method which is now being experimented upon on a large scale, known as the Bang and Ruffin process, is to shake up the diluted spirit with petroleum oils, which have the power of absorbing the fusel oil and so withdrawing it from the dilute alcohol.

5. MANUFACTURE OF ALCOHOLIC BEVERAGES FROM RECTIFIED SPIRIT.—Much of the rectified spirit, from whatever source derived, is used in connection with the manufacture of wines for fortifying them and in arresting fermentation at any desired stage. The so-called "silent spirit" made in England by the use of the Coffey still from grain-wort is largely utilized in the manufacture of factitious brandies and wines, and the same thing applies to the spirit manufactured in France from beet-roots and beet-root molasses, where it is made to supply the deficiencies in the wine and Cognac production. The composition of many of these factitious or imitation liquors will be spoken of in the next section in enumerating the products of this industry.

## III. Products.

1. RECTIFIED AND PROOF SPIRIT.—"Rectified spirit of wine" is the name given to the most concentrated alcohol producible by ordinary distillation. The British Pharmacopœia describes rectified spirit as containing eighty-four per cent. by weight of real alcohol and having a specific gravity of .838. The United States Pharmacopœia under the name "alcohol" simply calls for a spirit containing ninety-one per cent. of real alcohol and having a specific gravity of .820. The "spirit" of the German Pharmacopœia has a specific gravity of .830 to .834, and hence corresponds more nearly to the British "rectified spirit."

"Proof spirit" is a term in constant use in England for the purposes of excise, and its strength was defined by act of Parliament to be such that at 51° F. (10° C.) thirteen volumes shall weigh the same as twelve volumes of distilled water. The "proof spirit" so made will have a specific gravity of .91984 at 15.5° C. (60° F.) and contain, according to Fownes, 49.24 per cent. by weight of alcohol and 50.76 per cent. of water. Spirits weaker than proof are described as U. P. (under proof), stronger than proof as O. P. (over proof); thus, a spirit of fifty U. P. means fifty water and fifty proof spirit, while fifty O. P. means that the alcohol is of such strength that

to every one hundred of the spirit fifty of water would have to be added to reduce it to proof strength. Tables are in use which give for alcohol of a given specific gravity at 15.5° C. (60° F.) the corresponding percentage by weight, percentage by volume, and percentage of proof spirit contained. (See Wynter Blyth, Foods, Composition and Analysis, p. 371.)

2. ALCOHOLIC BEVERAGES MADE BY DIRECT DISTILLATION OF THE FERMENTATION PRODUCTS.—*Arrack.*—Any alcoholic liquor is called "arrack" in the East, but arrack proper is a liquor distilled either from toddy, the fermented juice of the cocoa-nut palm, or from malted rice. The arrack from Goa and Columbo is considered the best, and is made from toddy alone. This latter is gotten by the incision of the palm, and is collected in pots hung to the tree under the cuts. It is then fermented and distilled. In preparing the other variety, as carried out in Batavia and Jamaica, the rice is covered with water and allowed to germinate, dried at a temperature of 59° F., which arrests germination, and then a wort is made from the malted rice in the same manner as from malted grain, which is afterwards distilled. The commonest pariah arrack of India is generally narcotic, very intoxicating, and unwholesome. It is prepared from coarse jaggery sugar, spoilt toddy, refuse rice, etc., and rendered more intoxicating by the addition of hemp leaves, poppy-heads, juice of stramonium, and similar deleterious substances.

*Brandy* in its purest form (Cognac) is the direct product of the distillation of French wines. Its peculiar flavor and aroma are due to the presence of ethyl pelargonate (œnanthic ether). The better qualities of Cognac are distilled from white wines, the inferior varieties from the dark-red Spanish and Portuguese wines or from the marc or refuse of the wine-press, and called *eau de vie de marc.* A great deal is also entirely factitious, being mixtures of grain spirit and water to which different coloring and aromatic substances have been added. When first distilled, brandy, like other spirituous liquors, is colorless, when it is known as *white brandy*, and continues so if kept in glass- or stone-ware, but if stored in oak casks, as is usually the case, it gradually acquires a yellowish tint from the wood, and it is then termed *pale brandy.* The still deeper color which it frequently possesses is given it by the addition of caramel-color, which was originally designed to simulate the appearance of an old brandy long stored in casks. The coloring matter is also sometimes prepared from catechu and similar astringent and aromatic substances.

Numerous recipes for factitious brandies are furnished for the use of rectifiers in making up imitations of Cognac. Two such recipes are given:

No. 1.—Powdered catechu, 100 grammes; sassafras-wood, 10 grammes; balsam of tolu, 10 grammes; vanilla, 5 grammes; essence of bitter almonds, 1 gramme; well-flavored alcohol (at 85°), 1 litre.

No. 2.—Malt spirit (17 U. P.), 100 gallons; nitrous ether, 2 quarts; ground cassia-buds, 4 ounces; bitter almond meal, 5 ounces; sliced orris-root, 6 ounces; cloves in powder, 1 ounce; capsicum, 1½ ounces; good vinegar, 3 gallons; brandy-coloring, 3 pints; powdered catechu, 2 pounds; full-flavored Jamaica rum, 2 gallons. Mix in an empty Cognac-cask and macerate for a fortnight, with occasional stirring. Produces 106 gallons at 21 or 22 U. P.

*Kirschwasser* is a spirituous liquor obtained in the Black Forest and in Switzerland by the distillation of cherries. These are picked free from the

stalks and only the sound fruit taken. They are crushed for the extraction of the juice, and a portion of the cherry-stones are then separately crushed so as to bruise the kernels and returned to the juice. These bruised kernels impart the almond flavor to the product and give to it a small quantity of prussic acid (.15 gramme per litre in good kirsch and more in inferior kinds). After fermentation the liquor is drawn off and distilled by steam. The kirsch is colorless, of agreeable odor and flavor, which improves by keeping, and equal in strength to the strongest spirit.

*Rum* is a spirit obtained in the West Indies, notably in Jamaica, Martinique, and Guadeloupe, from the molasses of the sugar-cane by fermentation and distillation. The process of fermentation of the molasses as carried out in Jamaica has already been described. When new, rum is white and transparent, and has when freshly distilled an unpleasant odor, due to oils contained. These are got rid of by treatment with charcoal and lime. It owes its characteristic flavor to butyric ether, which compound is also prepared artificially on a large scale, and as rum essence is used with "silent spirit" to make a factitious rum. Rum is always colored artificially with caramel-color.

*Whiskey* is the spirit obtained from the fermented wort of corn, rye, and barley, either raw or malted. In Scotland and Ireland, malted barley, pure or mixed with other grain, is chiefly used; in the preparation of the Bourbon whiskey of Kentucky partially-malted corn and rye are taken, while for the Monongahela whiskey of Western Pennsylvania only rye (with ten per cent. of malt) is used.

The difference between the Irish and the Scotch whiskeys lies mainly in the fact that the former is distilled in the common or so-called pot-stills, which brings over together with the spirit a variety of flavoring and other ingredients from the grain, while in Scotland the Coffey still is used, the product of which is a spirit deprived of essential oils. The Irish "poteen" whiskey has a smoky flavor, due to the use of peat fires in preparing the malt. This flavor is imitated by the addition of one or two drops of creasote to the gallon of spirits.

3. Alcoholic Beverages made from Grain Spirit by Distillation under Special Conditions.—*Gin* is common grain spirit distilled and aromatized with juniper-berries, either when the "low wines" are concentrated or later, using full-strength spirit. The proportion employed is variable, depending upon the nature of the spirit; usually one kilogramme of berries is enough to flavor one hectolitre of raw grain spirit. The finest gin, known as "Hollands," is made in the distilleries of Schiedam, whence also the name "Schiedam Schnapps." Strassburg turpentine, oil of fennel, coriander and cardamom seeds are frequently substituted either wholly or in part for the juniper-berries, particularly in the English-made gin. The quality and healthfulness of the gin depends largely upon the purity of the spirit used in the distillation, whether raw or rectified.

It is obvious that many factitious brandies belong also in this class, being made by distillation of mixtures of which grain spirit is the basis and not by distillation of wine. These have already been described.

4. Liqueurs and Cordials.—Liqueurs is the name now given to such spirituous drinks as are obtained by mixing various aromatic substances, such as anise, absinthe, essence of orange-peel, etc., with brandy or alcohol. Most are obtained by steeping in pure brandy or spirit different fruits or aromatic herbs and submitting the resulting liquid to distillation. They

are then colored, and are usually sweetened with sugar. The best known of them, absinthe, contains a characteristic ingredient, oil of wormwood, to which its deleterious effects on the nervous system are supposed to be due. At the same time the amount of total essential oils held dissolved in the strongly alcoholic liquid are such that when diluted with water the solution becomes milky and turbid.

Among the liqueurs may be enumerated *Absinthe* (consumed chiefly in Paris), *Anisette* (made in the south of France), *Chartreuse* (made by the monks of the Grande Chartreuse Monastery near Grenoble), *Curaçoa* (originally made in Holland of Curaçoa oranges), *Maraschino* (made in Italy of Dalmatian cherries), *Ratafia* (made in France from a great variety of fruits), and *Usquebaugh* (a strong cordial made in Ireland. It furnishes the name from which the word whiskey is derived).

The composition of the several alcoholic liquors enumerated cannot be given in great detail, as their differences depend so largely upon the flavoring and aromatic ethers and essential oils, which are present in very minute quantities. Their general differences in alcoholic strength and the extract and ash of several are, however, given on the authority of König: *

| | Alcohol by volume. | Alcohol by weight. | | Alcohol by volume. | Alcohol by weight. |
|---|---|---|---|---|---|
| Russian Dobry wutky | 62.0 | 54.2 | Gin | 47.8 | 40.3 |
| Scotch whiskey | 50.3 | 42.8 | Ordinary German schnapps | 45.0 | 37.9 |
| Irish whiskey | 49.9 | 42 3 | Rum | 49.7 | 42.2 |
| English whiskey | 49.4 | 41.9 | French Cognac brandy | 55.0 | 47.3 |
| American whiskey | 60.0 | 52.2 | | | |

And in one hundred cubic centimetres of the following:

| | Specific gravity. | Alcohol by volume. | Alcohol by weight. | Extract. | Ash. |
|---|---|---|---|---|---|
| Arrack | 0.9158 | 60.5 | 52.7 | 0.082 | 0.024 |
| Cognac | 0.8987 | 69.5 | 61.7 | 0.645 | 0.009 |
| Rum | 0.9378 | 51.4 | 34.7 | 1.260 | 0.059 |

The composition of some of the well-known liqueurs is also given on the same authority: †

| | Specific gravity. | Alcohol by volume. | Alcohol by weight. | Extract. | Cane-sugar. | Other extractions. | Ash. |
|---|---|---|---|---|---|---|---|
| Absinthe | 0.9116 | 58.93 | . . | 0.18‡ | . . | 0.32 | . . . |
| Bonekamp of Maag bitters | 0.9426 | 50.0 | 42.5 | 2.05 | . . | . . | 0.106 |
| Benedictine bitters | 1.0709 | 52.0 | 44.4 | 36.00 | 32.57 | 3.43 | 0.043 |
| Ginger | 1.0481 | 47.5 | 40.2 | 27.79 | 25.92 | 1.87 | 0.141 |
| Crême de menthe | 1.0447 | 48.0 | 40.7 | 28.28 | 27.63 | 0.65 | 0.068 |
| Anisette of Bordeaux | 1.0847 | 42.0 | 35.2 | 34.82 | 34 44 | 0.38 | 0.040 |
| Curaçoa | 1.0300 | 55.0 | 47.3 | 28 60 | 28.50 | 0.10 | 0.040 |
| Kümmel liqueur | 1.0830 | 33.9 | 28.0 | 32.02 | 31 18 | 0.84 | 0.058 |
| Peppermint liqueur | 1.1429 | 34.5 | 28 6 | 48.25 | 47.35 | 0.90 | 0.068 |
| Swedish punch | 1.1030 | 26.3 | 21.6 | 36.61 | . . | . . | . . . |

* König, Nahrungs- und Genussmittel, vol. ii. p. 469.
† Ibid., p. 470. ‡ Oil of wormwood.

5. SIDE-PRODUCTS.—The distiller's residues (Schlempe, vinasse) form a side-product of considerable value as a cattle food because of its composition. It is especially rich in protein matter, fat, and non-nitrogenous extractive, or carbohydrates. The residues from the beet- and cane-molasses distillation, moreover, yield an ash very rich in potash salts, so that they constitute, especially in France, a very important source of potashes. The composition of several of these distillery residues are given in the moist state on the authority of König: *

| | Water. | Fat. | Nitrogenous matter. | Non-nitrogenous extract. | Cellulose. | Ash. |
|---|---|---|---|---|---|---|
| Rye-mash residues (ten analyses) . . . . . . | 93.48 | 0.22 | 1.40 | 4.05 | 0.52 | 0.33 |
| Potato-mash residues (six analyses) . . . . | 95.10 | 0.17 | 1.17 | 2.17 | 0.92 | 0.47 |
| Molasses residues . . . | 91.86 | . . | 2.04 | 4.56 | . . | 1.54 |

Two complete analyses of distillery residues dried by centrifugating and heating in kilns are given on the authority of Rosenbaum :†

| | Maize. | Potatoes. |
|---|---|---|
| Water . . . . . . . . . . . . . . . . . . . . | 11.62 | 7.83 |
| Ash . . . . . . . . . . . . . . . . . . . . | 6.50 | 16.40 |
| Crude proteid matter . . . . . . . . . . . . . . | 21.44 | 23.08 |
| Crude fibre . . . . . . . . . . . . . . . . . | 10.54 | 8.60 |
| Non-nitrogenous extractives . . . . . . . . . . . | 38.96 | 40.54 |
| Crude fat . . . . . . . . . . . . . . . . . . | 11.44 | 3.55 |
| | 100.00 | 100.00 |

Of these constituents the following were assimilable as food :

| | | |
|---|---|---|
| Albuminoids . . . . . . . . . . . . . . . . . | 17.20 | 18.50 |
| Carbohydrates . . . . . . . . . . . . . . . . | 37.40 | 39.40 |
| Fat . . . . . . . . . . . . . . . . . . . . | 9.10 | 2.85 |

## IV. Analytical Tests and Methods.

The most important determination in this class of beverages is the *alcoholic strength*. In the case of rectified or proof spirit, a simple specific gravity determination is all that is necessary, and then the percentage strength can be found from the alcohol tables that have been prepared. The determination should be made at 15.5° C. (60° F.), or if at another temperature, a correction in the reading must be made. By multiplying the number of degrees above or below 15° by .4 and adding the product to the percentage given by the table when the temperature is lower than 15°, or deducting it when the temperature is above, we get a correct result. In freshly-distilled and colorless whiskeys and brandies, in which the amount of extract is trifling, the alcoholic percentage can also be determined with sufficient accuracy by the specific gravity method. In such liquors as contain more extractive matter, like rum and the liqueurs and cordials, the

* König, Nahrungs- und Genussmittel, vol. ii. p. 468.
† Jahresber. der Chem. Technol., 1887, p. 1058.

alcohol must first be distilled off, and then made up to original volume with distilled water, as described on p. 212.

A process of estimating the alcohol by oxidizing it into acetic acid and determining this by volumetric soda solution has also been recommended by Dupré, but it can only be applied to a pure alcoholic distillate, and has no advantage over the specific gravity determination made on the same distillate. It is obvious that the Geissler vaporimeter and the several forms of ebullioscope (see p. 212) can be applied with rectified or proof spirit, but, as said before, they are not capable of the greatest accuracy.

The detection and determination of *fusel oil*, which is a persistent impurity in potato and grain spirit, is one of the most important tests to be made. To detect it, the greater part of the alcohol is distilled off at as low a temperature as possible, the residual liquid mixed with an equal amount of ether and well shaken. The ethereal layer is then separated and allowed to evaporate spontaneously, when amyl alcohol, if present, will be recognized in the residue by its smell and chemical characters. Petroleum-ether may be advantageously substituted for the ether in this test.

Marquardt dilutes forty cubic centimetres of the spirit with sufficient water to bring the density to about .980 and then agitates the liquid with fifteen cubic centimetres of pure chloroform. The chloroform is allowed to settle, separated, and, after shaking with an equal measure of water, is allowed to evaporate spontaneously. The residue is treated with a little water and one or two drops of sulphuric acid, and sufficient solution of potassium permanganate is then added to cause the mixture to remain red after standing for twenty-four hours in a closed tube. Shortly after adding the permanganate the odor of valeric aldehyde will be observable, but after standing only the odor of valeric acid is distinguishable. This can be recognized even when the original residue is almost odorless and the smell is not masked by the presence of essential oils, etc. Marquardt has devised a more elaborate modification of the test to serve for the quantitative determination of the fusel oil present. For the detailed description the reader is referred to Allen, 3d ed., vol. i. p. 154.

*Caramel* (burnt sugar) is used for coloring and flavoring spirits, and is left as a brown residue on evaporating the spirit on the water-bath. This residue is distinguished by its bitter taste, and if further heated it carbonizes and smells of burnt sugar.

*Tannin* is often present in brandy and whiskey, being chiefly extracted from the casks used in storing. Sometimes, as in factitious brandies, it is purposely added in the form of tincture of oak-bark. It may be detected by the darkening produced on adding ferric chloride to the spirit, and any reaction thus obtained may be confirmed by boiling off the alcohol from another portion of the spirit and adding solution of gelatine to the residual liquid, when a precipitate will be produced if tannin be present.

## *E.* BREAD-MAKING.

Bread-making as ordinarily conducted is to be classed as one of the fermentation industries, as the swelling of the dough which must precede the baking is generally accomplished by the aid of the alcoholic fermentation brought about by the addition of "leaven" or yeast. For every kilogramme of bread, on the average, 2.5 grammes of alcohol and 2.7 grammes of carbon dioxide gas are produced. Both are lost in the baking, but the carbon

dioxide gas when first generated is caught in the thick and viscid dough and causes it to swell up and become spongy in structure. This not only gives to the bread when baked a porous and cellular structure, but allows the chemical changes to take place throughout its entire substance, whereby it is made more readily digestible.

As the only effective result of the alcoholic fermentation is performed by the carbon dioxide, of course the addition of chemical mixtures liberating carbon dioxide gas in the dough may be made to obviate the necessity of using leaven or yeast, and similarly aerated breads may be made by simply forcing carbon dioxide under pressure into the dough.

A few varieties of bread are made from dough, baked without any aeration either natural or artificial, such as hard crackers, the unleavened bread of the Jews, the Scotch oat-cake, and the corn-cake of the Southern States. These exceptions are of relatively minor importance, and by far the largest amount of bread is prepared by the aid of a fermentation process.

## I. Raw Materials.

1. Flour.—This may be from either wheat, rye, barley, oats, maize, or Indian corn, and rice, although wheat flour is used in far the largest amount.

The average composition of the several cereals has already been given. (See page 169.) Wheat flour contains the following substances: starch, dextrine, cellulose, sugar, albumen, gliadin, or gluten, mucin, fibrin, cerealin, fat, mineral matters, and water. The first four are carbohydrates, or non-nitrogenous substances, and they form nearly three-fourths of the entire weight of the flour. The nitrogenous matter consists of at least five principles, three of which, gluten (or gliadin), mucin (or mucedin), and fibrin, constitute the bulk of the material known as crude gluten, which is the substance left when flour is kneaded with water and afterwards washed to remove the starch and any soluble substance. The remaining two nitrogenous principles, albumen and cerealin, are soluble in water, and are carried away with the starch in the process of washing. Crude gluten possesses a peculiar adhesiveness, arising from the presence of gliadin, which is a highly tenacious body, and which is not present in the same form in other cereal flours. It is this adhesive property which gliadin imparts to gluten that renders wheaten flour so well adapted for bread-making purposes.

The vegetable albumen mentioned above as soluble in cold water is accompanied also by small amounts of legumin, or vegetable casein, which is also soluble in water. The cerealin is a soluble nitrogenized ferment occurring especially in the husk or bran of wheat and other cereals. It has a powerful fermentative action on starch, rapidly converting it into dextrine and other soluble bodies. The presence of cerealin in bran renders "whole meal" unsuitable for making bread by fermentation with yeast, though it can be used with baking-powders, and "aerated bread" can be made from it. The cerealin acts like malt extract, causing a too rapid conversion of the starch into dextrine and sugar, and hence, although the bran is rich in nitrogenous food constituents and salts like phosphates, it is ordinarily separated from the flour. The difference in the composition of the several parts of the wheat-grain is seen in the following table given by Church :*

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* A. H. Church, Foods, etc., South Kensington Hand-book, pp. 63 and 64.

| | Fine White Flour. | | Coarse Wheat Bran. | |
|---|---|---|---|---|
| | In 100 parts. | In 1 pound. | In 100 parts. | In 1 pound. |
| Water | 13.0 | 2 ounces 35 grains. | 14.0 | 2 ounces 105 grains. |
| Fibrin, etc. | 10.5 | 1 " 297 " | 15.0 | 2 " 175 " |
| Starch, etc. | 74.3 | 11 " 388 " | 44.0 | 7 " 17 " |
| Fat | 0.8 | 0 " 57 " | 4.0 | 0 " 280 " |
| Cellulose | 0.7 | 0 " 49 " | 17.0 | 2 " 316 " |
| Mineral matter | 0.7 | 0 " 49 " | 6.0 | 0 " 422 " |

Of course, milling processes have to be specially adapted to the separation of these quite different parts of the wheat-grain, the white flour free from bran being sought. By the old-fashioned "low-milling" process, or grinding between stones placed very close together and bolting, it was impossible to obtain a flour entirely free from contamination. The advance to "high-milling" with stones far apart, allowing the middlings which were produced to be purified before grinding to flour, was a step which made it possible to make from winter wheat an excellent and pure flour. When, however, spring wheat with its hard and brittle outer coats became important commercially, it was necessary to resort to the roller methods of milling, which, in conjunction with peculiar purifying machinery, would furnish a flour free from all undesirable impurities. This latter process has now almost universally replaced the other in the newer mills.

While most of the other cereals before mentioned may be found occasionally in admixture with wheat flour, very few are used alone as substitutes for it. Rye flour is probably the only one. It makes a dark-colored, heavy and sourish bread, which, however, keeps moist a long time. It is much used in Germany and Northern Europe under the name of "black bread." A more palatable bread may be made from a mixture of two parts wheat flour and one part rye flour. This latter flour contains a slightly larger amount of fat and of mineral matter than wheat flour. It is never so white as wheat flour and the gluten has very little adhesive character. Ritthausen states that the gluten of rye flour consists chiefly of mucin (mucedin) and vegetable casein, and that gliadin is absent entirely.

2. Yeast, or Ferment.—The yeast is at present almost always added, either as brewer's yeast or compressed yeast. In former times (and to a considerable extent still in France) wheat bread was made by the use of *leaven*, which consists of a portion of dough left over from a previous baking, charged with the ferment and in part changed by its action. This leaven is originally gotten by allowing flour and water to start into spontaneous fermentation, the nitrogenous matters becoming soluble and attacking the starch and sugar. The leaven tends, however, to continue its decomposition and to pass from the alcoholic into the lactic fermentation. Hence, if the leaven is in the proper stage of decomposition, it will induce the alcoholic fermentation and generate carbon dioxide gas, raising the dough; if it be, however, in a more advanced state of decomposition, lactic fermentation will be induced and the bread will not raise, but become heavy and sour. In domestic practice, to avoid this latter result, salæratus (bicarbonate of potash or soda) is added to the dough. This neutralizes the lactic acid as fast as formed, and at the same time liberates carbon dioxide gas to inflate

the dough. An excess of this salt, however, makes the bread alkaline to the taste and yellow in color.

The black rye bread of Germany is also made with the aid of a leaven known as "sour dough." In this both the alcoholic and the lactic fermentations are in progress, the latter, however, preponderating. Four parts of such sour dough are used for one hundred parts of flour.

The brewer's yeast for bread-raising purposes must be a fresh and vigorous yeast-growth, as its value here depends largely upon the energy of the fermentation set up and the amount of gas given off. Its appearance and characters have been described before. (See p. 185.) Unless of the best quality, compressed yeast is to be preferred because of its reliability. The manufacture of this latter is carried out chiefly in connection with the spirit distilleries. At the time when the fermentation is most energetic, the yeast is skimmed off the surface and conveyed by wooden shoots to steam sieves, by which the husks are eliminated, the strained liquid passing on to the settling cisterns. When settled the surface liquid is drained off and sent for distilling purposes, and the yeasty sediment mixed with starch and put into the filter-presses, which squeeze out all the liquid, leaving a dough-like paste, which, when sufficiently dry, is packed into bags and packets and is ready for distribution. Yeast from its peculiar slimy nature cannot be pressed well, hence the addition of starch, which permits the removal of more of the liquid from the yeast. Absolutely pure yeasts do not keep so well as the same yeasts with an addition of from five to ten per cent. of starch. In high-class yeasts the quantity added is about five or six per cent.; it is often added in quantity beyond this as an adulterant. A good sample of compressed yeast has the following characteristics: It should be only very slightly moist, not sloppy to the touch; the color should be a creamy white; when broken it should show a fine fracture; when placed upon the tongue it should melt readily in the mouth; it should have an odor of apples, not like that of cheese; neither should it have an acid taste or odor. Any cheesy odor shows that the yeast is stale and that incipient decomposition has set in.

3. Baking-powders.—To obviate the necessity of using yeast and waiting until the dough should rise sufficiently under the influence of fermentation, it was early sought to supply the necessary carbon dioxide to the dough by chemical reactions. The earliest proposal was that of Liebig to use sodium bicarbonate and hydrochloric acid, which should evolve carbon dioxide and leave sodium chloride (common salt) in the dough. Next was proposed sodium bicarbonate and tartaric acid, or acid potassium tartrate (cream of tartar). More generally satisfactory than either of these was acid calcium phosphate (either alone or with acid magnesium phosphate), which with bicarbonate of soda formed Horsford's baking-powder. More objectionable was the introduction of alum with the sodium bicarbonate. Most of these baking-powder mixtures, then, have starch or flour added as "filling," and in amount varying from twenty to sixty per cent. Sesquicarbonate of ammonia is also used in many of the mixtures, replacing part of the bicarbonate of soda. *Self-raising flours* have these baking-powders already added to the flour in such proportions as will insure a spongy dough upon the simple addition of water and kneading into loaves.

## II. Processes of Manufacture.

1. The Mixing of the Dough and its Fermentation.—The mixing of the flour with water is not only for the purpose of bringing into solution the dextrine, the sugar, and the soluble albuminoids, and of allowing these latter as peptones to act upon the insoluble constituents of the flour, such as the gluten, but also to penetrate and soften the starchy material.

The yeast may be added directly along with the water to some of the flour to prepare a "sponge," from which the whole batch of dough is afterwards made, or a "ferment" may be made from the yeast with potatoes, which then is used to prepare the "sponge." In the latter case, potatoes are boiled and mashed with water into a moderately thin liquor, to which the yeast is added, and the fermentation is allowed to proceed for some time. In either case, whether the yeast is used direct or a potato ferment is first made, it is worked up with a portion of the flour into a slack dough, which constitutes the sponge, and is set to rise in a warm place. When the sponge has risen sufficiently the remainder of the flour is worked in with sufficient water to which some salt has been added, and the dough is made, kneaded, allowed to stand again to rise, and then prepared for baking.

The use of potato ferment is based upon the belief that the yeast-cells are strengthened by the soluble nitrogenous matter of the potato, which acts as a yeast stimulant and enables a smaller quantity of yeast to hydrolyze a larger amount of starch. The yeast-cells then act very rapidly upon the glucose so produced and develop the alcoholic fermentation. The albuminoids of the flour are also softened and partially peptonized, and these changed albuminoids in turn assist in the hydrolysis of the starch.

2. Baking.—For baking, the oven should have a temperature of 400° to 450° F. (200° to 230° C.). Before putting the loaves in, they are often wetted on the surface so as to assist in the prompt formation of a crust that shall prevent the dough from expanding too rapidly. The heat expands the gases throughout the loaf and so swells it and vaporizes a portion of the moisture. The action of the heat and steam soon converts the starch on the surface of the loaf into dextrine and maltose, and these at the high temperature are slightly caramelized, thus giving the crust its brownish color. At the temperature of the interior of the loaf (212° F. or slightly above) the starch-cells will have burst, the coagulable albuminoids will have been coagulated, and their diastatic power entirely destroyed.

Steam is often injected into the oven during the baking. The effect is to produce a glazed surface on the outside of the crust. It not only dextrinizes and glazes the crust, but keeps the interior of the loaf moist by preventing too rapid evaporation. Of course, in perfectly tight ovens the steam resulting from the evaporation of the moisture of the bread is kept in, and soon acts in the same manner though in a lesser degree.

One hundred kilogrammes of flour will yield, according to its quality, from one hundred and twenty-five to one hundred and thirty-five kilos. of bread.

3. Use of Chemicals Foreign to the Bread.—Both alum and sulphate of copper (and notably the former) have been used in baking bread from inferior or unsound flours in order to improve the appearance of the bread. This they do by preventing or lessening the breaking up of the gluten and starch during fermentation, and so cause a loaf made from a bad

flour to be larger, less sodden, and whiter, giving it the appearance of having been made from better flour. As these chemicals are injurious to health, and as their sole purpose is to allow of deception as to the character of the flour used in bread-baking, they ought to be prohibited by law.

Liebig suggested the use of lime-water as a means of retarding too rapid decomposition of the starch during the fermentation of bread-making. The bread made with the proper amount of lime-water is said by Jago* to be more spongy in texture, pleasant in taste, and quite free from sourness. In the bread the lime exists as calcium carbonate, but in such quantities as to be perfectly harmless. The use of lime-water in bread-making is said to be practised extensively by Glasgow bakers.

## III. Products.

1. BREAD.—The nature of the change which the flour undergoes in the bread-baking process has already been indicated in part. The composition of the finished bread can now be noted. A loaf of wheaten bread consists of two parts, the *crumb* and the *crust*, which differ somewhat in both physical and chemical character. The crumb is white in color, more or less vesicular in structure, soft when fresh, and of agreeable taste and sweet odor; the crust is harder, more easily broken, of a chestnut-brown color, and nearly destitute of all porous character, is sweeter in taste, because of the greater change of the starch into dextrin and maltose. The chemical differences between the crumb and crust of wheat bread are shown in several of the analyses given by Von Bibra.†

| | Calculated for Anhydrous Bread. | | | | | Water originally contained in the bread. |
|---|---|---|---|---|---|---|
| | Nitrogenous material. | Dextrin and soluble starch. | Sugar. | Fat. | Starch. | |
| Wheaten bread, Nürnberg, crumb | 11.296 | 14.975 | 4.175 | 1.683 | 67.871 | 40.600 |
| Wheaten bread, Nürnberg, crust. | 10.967 | 16.092 | 4.149 | 0.715 | 68.077 | 13.000 |
| Rye bread, Nürnberg, crumb . . | 17.096 | 15.418 | 2 618 | 1.064 | 63.814 | 46.440 |
| Rye bread, Nürnberg, crust . . . | 14.838 | 18.275 | 4.835 | 0.564 | 60.842 | 12.449 |
| Wheaten bread from Madrid . . | 8.064 | 4.763 | 1.470 | 1.173 | 84 530 | 15.000 |
| Wheaten bread from years 1816 and 1817 . . . . . . . . . . . | 8.541 | 10.192 | 2.184 | . . . | 79.083 | 11.666 |
| Pumpernickel from Westphalia (contained some bran) . . . . | 7.354 | 14.531 | 4.953 | 4.233 | 68.929 | 9.160 |
| Wheaten Zweiback, Hamburg . . | 11.296 | 4.363 | 2.145 | 0.824 | 81.372 | 11.420 |
| Rye Zweiback, Bremen . . . . . | 13.296 | 12.209 | 7.035 | 1.360 | 66.100 | 14.000 |
| Barley bread from Lower Bavaria | 6.387 | 5.497 | 4.420 | 0.566 | 83.130 | 11.780 |
| Oaten bread from Bavaria (perfectly free from adulteration) . | 9.741 | 4.653 | 2.846 | 10.948 | 71.812 | 8.660 |
| Fine rye bread from Dalecaria (containing bran) . . . . . . | 10.903 | 28.269 | 6.345 | 0.807 | 53.676 | 18.333 |

The differences between wheat bread made by the usual fermentation process and wheat bread aerated by carbon dioxide under pressure (Dauglish system) are shown also in the following analyses by Dr. Bell:‡

* Chemistry of Wheat, Flour, and Bread, etc., 1886, p. 326.
† Stohmann and Kerl, Angewand. Chem., 4th ed., p. 215.
‡ Analyses and Adulteration of Foods, p. 131.

| Constituents of the Bread reduced to Dry State. | Aerated Bread. | | | | Home-made Bread. | | | |
|---|---|---|---|---|---|---|---|---|
| | Tin loaf. | | Cob loaf (Paris bread). | | Tin loaf. | | Cob loaf (Paris bread). | |
| | Crumb. | Crust. | Crumb. | Crust. | Crumb. | Crust. | Crumb. | Crust. |
| Starch, dextrine, cellulose, etc | 78.93 | 78.96 | 82.75 | 82.82 | 78.12 | 77.62 | 82.05 | 83.42 |
| Maltose . . . . . . . . . . | 6 40 | 5.61 | 4.66 | 3.94 | 6.87 | 6 68 | 4.85 | 4.11 |
| Nitrogenous matter, insoluble in alcohol . . . . . . | 10.30 | 11.28 | 8.58 | 9.09 | 11.65 | 11.17 | 10.59 | 8.68 |
| Nitrogenous matter, soluble in alcohol . . . . . . . . . | 1.96 | 1.75 | 1.80 | 1.85 | 1.74 | 2.00 | 1.28 | 2.37 |
| Fat . . . . . . . . . . . . | 0.18 | 0.16 | 0 13 | 0.17 | 0.22 | 1.22 | 0.15 | 0.39 |
| Inorganic matter or ash . . . | 2.23 | 2.24 | 2.08 | 2.13 | 1.40 | 1.31 | 1.08 | 1.03 |
| Percentage of moisture in bread when new . . . . . | 44.09 | 19.19 | 41.52 | 16.48 | 42.02 | 22.92 | 41.98 | 20.02 |

2. Crackers and Hard Biscuit are made from a dough composed of flour and water, with the addition in special cases of a great variety of sweetening and flavoring ingredients, such as milk, eggs, sugar, butter or lard, spices, and flavoring essences. The dough prepared in large masses is passed between rollers, and from the sheet of dough so obtained by other machines are cut out the various forms desired. Sheets or trays of these dough-forms pass by automatic machinery into and through long ovens at a regulated rate of speed, which can be so controlled as to give them exactly the requisite exposure to the heat needed for baking.

## IV. Analytical Tests and Methods.

1. For the Flour.—The *moisture* is determined by drying five grammes of the flour in a water-oven until constant weight is obtained.

The *starch* is estimated from the amount of glucose which is produced from it by the action of dilute acid. Two grammes of the flour are boiled in a flask with inverted condenser for several hours with some twenty cubic centimetres of sulphuric acid suitably diluted. When the conversion of the starch is completed the solution is neutralized with soda, made up to definite volume with water, and the glucose determined with Fehling's solution either gravimetrically or volumetrically, as described under glucose. (See p. 159.) After deduction of the sugar found in a previous test to be contained in the sample, the difference is the amount produced from the starch, together with a small quantity from the dextrine and traces of fibre. One hundred parts of glucose correspond to ninety of the starch.

To determine the *cellulose*, a weighed quantity of the flour is boiled with rather dilute sulphuric acid for ten minutes to dissolve the starch. A large quantity of water is then added, and the undissolved part allowed to settle. The residue is thrown upon a filter, well washed with boiling water, and then digested with dilute potash solution to dissolve the albuminous matter. It is then washed upon a tared filter, dried, and weighed. It is now incinerated and the ash determined. This subtracted from the weight of material on the tared filter gives the cellulose or fibre.

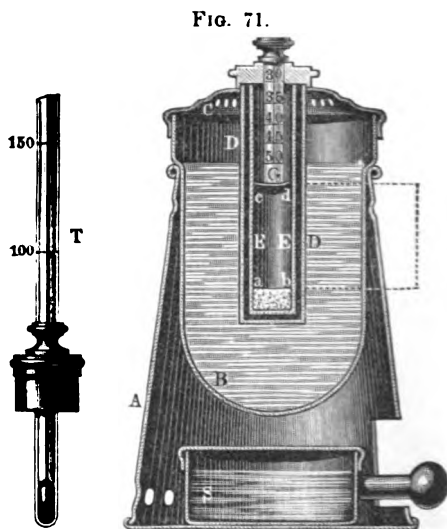
To determine the *sugar*, ten grammes of the flour or powdered grain are

repeatedly digested in alcohol of seventy per cent. and the filtrate made up to a bulk of three hundred cubic centimetres. This solution is first tested directly for glucose, but generally with negative results. A known portion of the filtrate is then boiled for four minutes with five cubic centimetres of normal sulphuric acid, neutralized with soda and tested with Fehling's solution, and the sugar present reckoned as cane is calculated from the result.

The total *nitrogenous compounds*, and the portions soluble or insoluble in alcohol, are generally determined. Sometimes the portions of the nitrogenous compounds soluble or insoluble in water are determined instead. In the latter case Wanklyn's ammonia process (see p. 199) is the most convenient. Generally, however, the distinction made is into those albuminoids soluble and those insoluble in alcohol. For this determination ten grammes of the flour are completely exhausted with eighty per cent. alcohol at a temperature of 140° F. (60° C.) and an aliquot portion of the total filtrate evaporated to dryness and weighed. A known quantity of this residue is then analyzed for nitrogen by the Dumas process with copper oxide, and the nitrogen so obtained multiplied by 6.3 gives the albuminoids. The flour left after treatment with alcohol is dried, and a weighed portion analyzed for nitrogen and similarly calculated for albuminoids (albumen and fibrin). For another process for these albuminoid determinations by Graham, see Allen, "Commercial Organic Analysis," 2d ed., vol. i. p. 366.

The *gluten* is best determined as recommended by Wanklyn and Cooper.* Ten grammes of the flour are mixed on a porcelain plate with four cubic centimetres of water so as to form a compact dough. This is placed in a conical test-glass or measure, fifty cubic centimetres of water added, and the dough manipulated with a spatula so as to free it from starch. The water is decanted off, a fresh quantity added, and the kneading continued until the water remains colorless. The gluten mass is then removed, kneaded in a little ether, and spread out in a thin layer on a platinum dish, where it is dried by the aid of a water-oven until the weight is constant. The crude gluten contains ash equal to about .3 per cent. on the flour and fat equivalent to 1.00 of the flour.

FIG. 71.

An examination of the crude gluten as to its power of distending under the influence of heat is often made as a means of judging of the value of a flour for bread-making. This is done by the aid of the *aleurometer* of Boland, shown in Fig. 71. Some thirty grammes of the flour are kneaded as just described, and seven grammes of the freshly-separated crude gluten obtained is placed in the inner vessel as shown at *a b*. In the mean time, while the gluten is being prepared, the tube *D* is heated by means of an oil-bath until

* Bread Analysis, London, 1886, p. 43.

the thermometer *T*, which is at first sunk in the tube *D*, registers 150° C. The thermometer is then withdrawn and the aleurometer *E*, containing the gluten, put in its place. The spirit-lamp under the oil-bath is allowed to burn for ten minutes longer and then extinguished. The piston *G* is graduated so that when pushed down it registers 25°. When the gluten swells and fills the space from *a b* to *c d* it touches the bottom of the piston and is at 25°. If it continues to swell the reading may be 30° or 35°, as shown on the scale when the piston is pushed up. If the gluten does not indicate at least 25° on the aleurometer it may be considered unfit for bread-making. A similar instrument, termed an *aleuroscope*, has been invented by Sellnick.

To determine the *fat* of the flour, four grammes are dried and repeatedly digested with ether until exhausted. The filtrates are evaporated in a tared vessel and weighed.

To determine the *ash*, ten grammes of the flour are incinerated in a platinum capsule to a white ash, which is then weighed.

Among the adulterations of flour, besides the admixture of other starchy material of lesser value, which must be looked for with the microscope (see starches, p. 168), the most frequently occurring is *alum*. For the detection of this, one of the best known tests is based upon the property of alumina of forming a violet- or lavender-colored lake with the coloring matter of logwood. Ten grammes of the flour should be mixed in a wide beaker with ten cubic centimetres of water, one cubic centimetre of the logwood tincture (five grammes of logwood-chips digested with one hundred cubic centimetres of strong alcohol) and an equal measure of a saturated aqueous solution of ammonium carbonate are then added, and the whole mixed together thoroughly. If the flour is pure, a pinkish color, gradually fading to a dirty brown, is obtained; whereas if alum be present, the pink is changed to a lavender or actual blue. As a precaution, it is desirable to set the mixture aside for a few hours or to warm the paste in the water-oven for an hour or two and note whether the blue color remains.

Or to separate any alum from the flour before applying the test, the flour is shaken up with chloroform in a stoppered glass cylinder provided with a stopcock below. After shaking the flour rises to the surface, while any foreign mineral matter settles at the bottom, and may be run off with a little of the liquid. The mineral matter is warmed and the chloroform gotten rid of by the aid of a current of air. It can then be examined. Any alum in it will of course be soluble in water, and can be shown by the usual tests. Methods for the quantitative determination of alum found as an adulterant in flour have been proposed by Dupré and Bell and by Wanklyn, for an account of which the reader is referred to Bell's work on the "Analyses and Adulteration of Foods."

2. For Bread.—The methods just described under flour are almost all equally applicable to the baked bread. To test bread for adulteration from alum a slightly different procedure is to be followed. To about a wine-glassful of water in a porcelain capsule five cubic centimetres of freshly-prepared tincture of logwood and the same quantity of the carbonate of ammonia solution are added. A piece of the crumb of the bread, say about ten grammes, is then soaked therein for about five minutes, after which the liquid is poured away and the bread is dried at a gentle heat. If alum be present the bread will acquire a lavender color or more or less approaching dark blue, according to the quantity of the alum which has been added; whereas if the color be a dirty brown, the bread may be regarded as pure.

## F. THE MANUFACTURE OF VINEGAR.

Under the general heading of fermentation mention was made of the acetic fermentation, which frequently follows the alcoholic fermentation. It is produced, it is true, by other species of ferments, but largely upon materials susceptible to the alcoholic fermentation or already changed by it into alcohol-containing products. The close association in nature of these two changes is readily understood when the chemical relationship of alcohol and acetic acid is looked at. The latter is the simple oxidation product of the former, and the processes for developing the alcoholic change in any sugary liquid, such as a beer-wort or a grape-must, have to be controlled carefully that they do not allow of this supplementary change whereby the alcohol goes over into acetic acid. The conditions under which the acetic fermentation sets in may be summarized as follows:

1. A liquid weak in alcohol, containing not more than twelve per cent. by weight of this compound.
2. Abundant access of air.
3. A temperature of from 20° to 35° C. (68° to 95° F.).
4. Acetic ferments (*Mycoderma aceti*, etc.), together with the food necessary for these organisms. Under this heading of acetic ferments Nägeli distinguishes, besides the *Mycoderma aceti*, the *Mycoderma cerevisiæ* and *Mycoderma vini*, although the latter of these is said by De Seynes to arrest the growth of the acetic ferment proper. Hansen also mentions a second ferment as found at times in beer along with the *Mycoderma*, or, as it is often termed now, *Bacterium aceti*, to which he gives the name *Bacterium Pasteurianum*.

The acetic ferment, as before stated (see p. 184), develops not by the budding process characteristic of the yeast ferment, but by splitting or fissure of the elongated cell. When these germs, which originally drop from the air, like the yeast-cells, into the fermenting or sugary liquids, find a liquid specially suited for their growth, as, for example, a mixture of wine and vinegar, they develop rapidly over the surface of the liquid, where they have the necessary oxygen supply, and form a gelatinous skin, which thickens and falls to the bottom of the vessel because of its increasing weight. Another skin forms at once again, and this in turn is replaced by a third, and so on until the liquid is completely exhausted of assimilable material. This skin, called the "mother of vinegar," consists of a multitude of these minute fissure ferments.

### I. Raw Materials.

Only such materials will be considered here as give rise to a vinegar by the normal acetic fermentation. The manufacture of acetic acid and technically important acetates will be spoken of later under pyroligneous acid as derived from the destructive distillation of wood.

The materials referred to as furnishing vinegar under the influence of the acetic fermentation are, first, wine; second, spirits; third, malt-wort or beer; fourth, fermented fruit juices other than wine; and, fifth, sugar-beets.

The *wines* used are both red and white wines, and are such as are of inferior vintages, and considered unfit for drinking as wine. Such wines are gathered together from all sections and are made into vinegar largely in France at Orleans and at Paris. The wines do not exceed ten per cent.

alcoholic strength. Wines about a year old are the best for vinegar-making, as the new wines are prone to undergo putrid or ropy fermentation, and older wines do not contain sufficient extractive matter.

The *spirits* used are chiefly the potato brandy of Germany and whiskey in this country, the vinegar in either case being made by the "quick vinegar" process. These spirits, when used for vinegar-making, are so diluted with water and vinegar already formed that the alcoholic strength ranges between three and ten per cent.

The *malt-wort* used for vinegar-making is exactly like that prepared for grain spirit manufacture, unmalted grain and malt being used admixed, and the alcoholic fermentation being pushed so as to produce the maximum amount of alcohol from the converted starch of the grain. When the alcoholic fermentation is completed it is allowed to stand for some days in the fining-vats, where all dead yeast and cloudiness subside, and it is then made to pass through a filter-bed of wood-chips into the acetifier. The unmalted grain used in the preparation of the wort must be thoroughly dried in a kiln previous to crushing in order that many of the glutinous and albuminoid matters may be destroyed. These would otherwise interfere with the keeping qualities of the vinegar. Sour ale or beer is said not to yield good vinegar, but a product very liable to undergo putrid fermentation, a very disagreeable smell being imparted to the vinegar in consequence.

*Cider* from apples and *Perry* from pears are about the only fruit juices besides wine fermented for the production of vinegar. Cider from good, sweet, and ripe apples serves for the manufacture of cider vinegar in this country. The cider is the product of a spontaneous alcoholic fermentation of the apple juice, and the vinegar formation is merely a continuation of this spontaneous change. Perry vinegar is made to some extent in England, and a vinegar from crab-apples in Wales.

*Sugar-beets* are used somewhat in France for vinegar-making. The beets are rasped to a fine pulp and pressed. The juice is diluted with water and boiled. After cooling, yeast is added and the alcoholic fermentation developed, and this product mixed with vinegar and treated as the other alcoholic liquids before mentioned for the development of the acetic fermentation.

Artificial glucose, cane-sugar, and molasses have also been used in England for the production of vinegars which are used to adulterate malt vinegar.

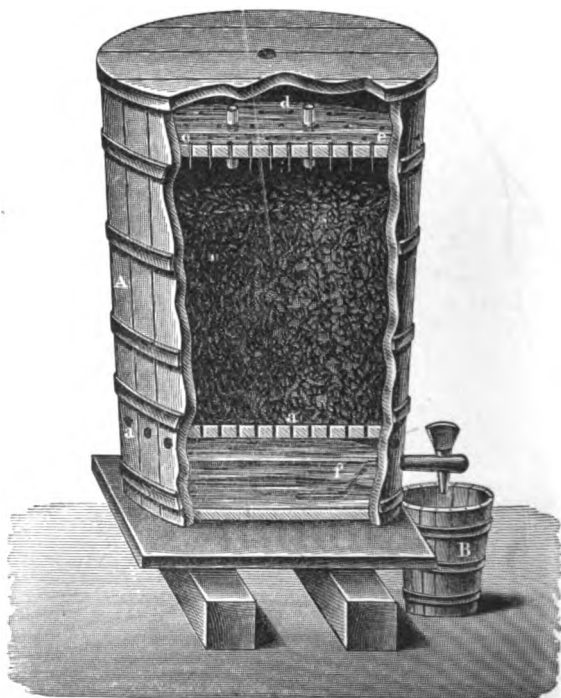
## II. Processes of Manufacture.

1. The Orleans Process.—This is the process by which wine vinegar is made in France and Germany, and is the oldest in practical use of the several methods now employed. The wine which is to be acetified is allowed to stand for a time over wine-lees, and then clarified by being passed through vats containing beech-shavings. The oaken acetifying vessels, holding from fifty to one hundred gallons, and known as "mother-casks," are first steamed out and then soured with boiling vinegar, which is made to fill one-third of the cask. The wine is now added in instalments of ten litres every eight days until the cask has become more than half-full, when one-third of its contents are siphoned off into storage-vats and the periodical addition of wine continued as before. The "mother-casks," or acetifiers, can be used in this way continuously for years until the sediment of yeast, argols, and impurities makes it necessary to give them a thorough cleaning. The vin-

egar obtained in this way has a very agreeable aroma, that made from white wines being most esteemed. When the wines employed in the Orleans process are too weak it often happens that the vinegar is ropy and wanting in transparency. In such case it must undergo the firing process. The progress of the acetification is judged of by plunging in a rod and examining the froth upon it when withdrawn. This should be white and copious. The temperature that is found to answer best is between 24° and 26.6° C. (75° and 80° F.)

Hengstenberg has proposed a modification of the Orleans process, whereby a series of the "mother-casks" are connected together at the base by short pieces of glass tubing. After the acetification of the first addition of wine in each cask the new wine is added only to the first cask, into which it runs slowly, while from the last cask of the series, by means of a siphon-tube fixed in the side, the excess flows off as finished vinegar. The increase of yield by this modification is, however, only slight.

2. The Quick-vinegar Process.—This process was first introduced by Schutzenbach in 1823, and has been considerably improved since. It is used exclusively in the case of spirit vinegar in Germany and in this country, and, with slight modifications, in England for malt vinegar. The vinegar-formers are upright casks from six to twelve feet in height and three to five feet in diameter. About a foot above the true bottom of the cask it has a false bottom perforated like a sieve. Upon this beech-wood shavings are heaped, extending nearly to the top of the cask. Between the true and false bottoms and just under the latter a series of holes is bored in the cask in a direction slanting downward and extending around the entire cask. The beech-shavings are first boiled in water and dried. They are then soured or soaked in warm vinegar for twenty-four hours, filled into place and covered by a wooden disk perforated by fine holes in which pack-thread is loosely filled. This disk also is perforated by four larger glass tubes open at both ends, which serve as air-vents. The cask is then closed on top by a wooden cover with a single hole in the centre, through which the alcoholic liquid is to be poured and from which air may escape. The entire arrangement may be understood from Fig. 72. During the oxidation of the

Fig. 72.

alcoholic liquid considerable heat is developed, and a current of air is thus made to enter through the circle of holes under the false bottom and rise through the wet shavings, escaping through the opening at the top. The diluted spirits or mixture to be acetified are poured into the top of each vat, and as they flow off, by the aid of a siphon arrangement from the base they are introduced into the top of the second vat. If not over four per cent. of alcohol were contained in the original liquid, that drawn off from the second vat will be converted into good vinegar. The temperature of the vinegar-forming casks should be about 35° C. (95° F.). Above this there is too much loss of alcohol and aldehyde by evaporation; below it, the oxidation goes too slowly. If the minute organisms known as "vinegar eels" show themselves, hot vinegar is poured in on top until it shows a temperature of 50° C. (122° F.) on running off, which kills them.

Whiskey, brandy, and grain spirit properly diluted are all acetified by the aid of this quick-vinegar process. To these diluted spirits a small amount of malt infusion is generally added to furnish nutritive matter for the development of the acetic ferment, which in this process as in the preceding is the agency whereby the atmospheric oxidation becomes effective in changing alcohol into acetic acid.

3. Manufacture of Malt Vinegar.—This is effected by a process much resembling the quick-vinegar process. The acetifiers are, however, much larger, holding from eight thousand to ten thousand gallons. Their construction is shown in Fig. 73. Bundles of birch-twigs, *B*, are supported upon a perforated bottom, from which the liquid trickles in fine streams. The malt-wort fed in below is warmed by a closed steam-coil of block-tin, and pumped to the top of the casks, where it is sparged, or sprinkled, in fine streams over the birch-twigs, and the process repeated until the vinegar shows the requisite strength. These birch-twigs have been previously freed from all juice and coloring matter by repeated boiling with water, and are soured before starting the sparging. The entire process of making malt vinegar requires about two months. The temperature at the beginning of the process is about 43° C. (110° F.), and later is kept at 38° C. (100° F.).

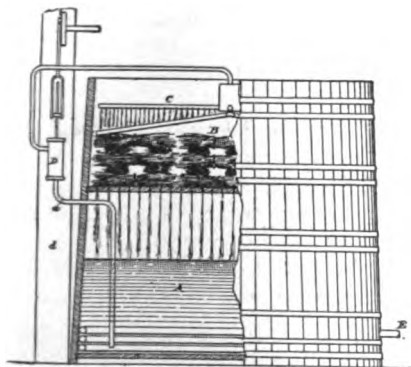



Fig. 73.

4. The Manufacture of Cider Vinegar.—As before stated, this is largely a spontaneous fermentation. The fresh cider is allowed to ferment in barrels having the bung-hole open, which are exposed to the sun or placed in a warm cellar. The acetification is often made a progressive change by adding fresh quantities of cider to the barrel every few weeks; the addition of "mother of vinegar" also is made to accelerate the change.

5. Pasteur's Process for Vinegar-making by Direct Use of the Vinegar Fungus.—Pasteur takes an aqueous liquid containing two per cent. of alcohol and one per cent. of vinegar and small amounts of phosphates of potassium, magnesium, and lime, and in this propagates the acetic ferment (*Mycoderma aceti*). The plant soon spreads out and covers the

whole surface of the liquid, at the same time acetifying the alcohol. When one-half of the alcohol has been changed small quantities of wine or alcohol mixed with beer are added daily until the acetification slackens, when the vinegar is drawn off and the "mother of vinegar" collected, washed, and used again with a freshly-prepared mixture. When wine or beer are used, the addition of the phosphate salts as food for the plant is unnecessary, but when pure alcohol is used they are needed. Vinegar prepared by this process is said to possess the agreeable aroma of wine vinegar.

## III. Products.

*Wine Vinegar* varies in color from light yellowish to red, according as it has been derived from white or red wines, that from the former being the most highly esteemed. The vinegar from red wines, however, can be decolorized by filtration through purified bone-black. Skimmed milk is also used for the same purpose. When thoroughly agitated with the vinegar the casein coagulates and carries down with it the greater part of the coloring matter of the vinegar, besides clarifying it. It is not used, however, so much as the filtration through charcoal. Wine vinegar has a specific gravity 1.014 to 1.022, and contains from six to nine per cent. (rarely twelve) of absolute acetic acid. When freshly made, it contains traces of alcohol and aldehyde. The amount of acid potassium tartrate (tartar) contained in wine vinegar averages .25 per cent. Its presence is peculiar to this variety of vinegar.

*Malt and Beer Vinegars* have a higher specific gravity (1.021 to 1.025), and contain dissolved dextrin, maltose, soluble albuminoids, and similar constituents of the malt extract. This kind of vinegar on evaporation leaves a glutinous residue only sparingly soluble in alcohol. It contains from three to six per cent. of acetic acid.

*Spirit Vinegar* is colorless as produced, but is frequently colored with caramel-color to imitate the appearance of wine or cider vinegar. It contains from three to eight per cent. of acetic acid, although the so-called "vinegar essence" (double vinegar) may contain as much as fourteen per cent.

*Cider Vinegar* is yellowish-brown, has an odor of apples, a density of 1.013 to 1.015, and contains from three and a half to six per cent. of acetic acid. It is distinguished from the other varieties by yielding on evaporation a mucilaginous extract smelling and tasting of baked apples and containing malic acid, which replaces the tartaric acid of the wine vinegar. The differences between cider vinegar and whiskey vinegar as manufactured in this country are shown in the accompanying analyses by Battershall :*

| | Cider vinegar. | Whiskey vinegar. |
|---|---|---|
| Specific gravity | 1.0168 | 1.0107 |
| Specific gravity of the distillate from neutralized sample | 0.9985 | 0.9973 |
| Acetic acid | 4.66 | 7.36 |
| Total solids | 2.70 | 0.15 |
| Total ash | 0.20 | 0.038 |
| Potassa and phosphoric acid in ash | Considerable. | None. |
| Heated with Fehling's solution | Copious reduction. | No reduction. |
| Treated with basic lead acetate | Flocculent precipitate. | No precipitate. |

*Glucose, or Sugar, Vinegar,* prepared from different saccharine and amylaceous materials by conversion with dilute acid, followed by fermenta-

* Food Adulteration and Detection, New York, 1887, p. 230.

tion and acetification, contains dextrose, dextrin, and often calcium sulphate (from commercial glucose). It is said to be employed in France and England for adulterating wine or malt vinegars.

*Factitious Vinegars* are often made from pyroligneous acid flavored with acetic ether and colored with caramel-color. Such a product differs from malt vinegar in containing no phosphates, and from wine or cider vinegar in the absence of tartaric or malic acids respectively.

## IV. Analytical Tests and Methods.

The determination of the *acetic acid* is usually done by titration with standard alkali, using phenolphthaleïn as indicator. In the presence of free sulphuric acid, it is necessary to distil a measured quantity of the sample almost to dryness and titrate the distillate, it being assumed that eighty per cent. of the total acetic acid present passes over.

The determination of the *extract* or solid residue in vinegar is executed in the same manner as described under beer or wine.

The test for *sulphuric acid* is an important one. In England, the manufacturers were allowed by law to add one part of sulphuric acid by volume to one thousand of vinegar in order to protect weak vinegar from the putrid fermentation. This addition is not necessary in good vinegar and is not generally followed at present. Still, it may be present, and is to be looked for in all vinegars. The usual test with basic chloride is inoperative here, as sulphates may be present in the vinegar from the water used, etc. Hehner's test for *free mineral acids* (sulphuric and hydrochloric), now regarded as satisfactory in this case, is based on the fact that acetates and most other salts of organic acids are decomposed by ignition into carbonates, having an alkaline reaction to litmus, while sulphates and chlorides of the light metals are unchanged on ignition and possess a neutral reaction. To determine the amount of free mineral acid it is sufficient therefore to carefully neutralize the vinegar with standard solution of soda before evaporation to dryness (the same process serving for a determination of the total free acid), ignite the residue, and titrate the aqueous solution of the ash with standard acid. If the free acid originally present were wholly organic, the ash will contain an equivalent amount of alkaline carbonate, which will require an amount of standard acid for its neutralization exactly equivalent to the amount of standard alkali originally added to the vinegar. Any deficiency in the amount of standard acid required for neutralization is due to the *free mineral acid* originally present in the vinegar.

The *tartaric acid*, a normal constituent of wine vinegar, may be tested for by evaporating to dryness and treating the extract with alcohol, which dissolves nearly everything but the tartar or acid potassium tartrate. On pouring off the alcohol and dissolving this in a little hot water its nature can be easily shown by the usual tests for tartaric acid.

*Caramel* is recognized by extracting the solid residue with alcohol and evaporating the solution to dryness; in its presence the residue now obtained will possess a decidedly dark color and a bitter taste.

*Metallic impurities*, such as lead, copper, and zinc, are at times to be found arising from the use of metallic vessels for storing the vinegar. Arsenic has also been found as an impurity through the use of impure sulphuric or hydrochloric acid. They are all detected by the usual qualitative tests.

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## STATISTICS.

#### I. PRODUCTION OF HOPS THROUGHOUT THE WORLD.

The hop crop of the world for the years 1892 and 1893 is thus given by Barth & Sons, of Nuremberg (U. S. Consular Report, Nov., 1893):

| | 1892. | 1893. |
|---|---|---|
| Germany | 49,029,200 pounds. | 24,800,000 pounds. |
| France | 4,700,000 " | 2,400,000 " |
| Bohemia | 9,000,000 " | 11,500,000 " |
| Remainder of Austria | 3,000,000 " | 3,000,000 " |
| Belgium and Holland | 7,400,000 " | 8,000,000 " |
| Russia | 4,500,000 " | 6,500,000 " |
| Great Britain | 41,000,000 " | 35,000,000 " |
| America | 36,500,000 " | 38,500,000 " |
| Australia | 1,600,000 " | 1,500,000 " |
| | 156,729,200 " | 131,200,000 " |

The United States imports a limited quantity of hops, but exports a much larger amount. The figures for recent years were:

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| Imports, in pounds | 2,772,045 | 3,017,821 | 2,375,922 | 1,319,319 |
| Valued at | $600,419 | $629,987 | $648,155 | $591,755 |
| Exports, in pounds | 16,765,254 | 11,426,241 | 17,161,669 | 21,145,512 |
| Valued at | $1,478,919 | $1,304,183 | $2,642,779 | $3,626,144 |

### II. *a*. DEVELOPMENT OF THE BEER PRODUCTION IN THE UNITED STATES.

According to the reports of the Commissioner of Internal Revenue, there were brewed in the United States the following amounts of malt liquors

| | 1897. Barrels (31 gals.). | 1898. Barrels (31 gals.). | 1899. Barrels (31 gals.). |
|---|---|---|---|
| New York | 9,493,620 | 10,093,450 | 9,680,308 |
| Pennsylvania | 3,902,301 | 4,245,972 | 4,299,116 |
| Illinois | 3,244,896 | 3,601,163 | 3,550,560 |
| Wisconsin | 2,673,948 | 2,886,502 | 2,846,233 |
| Ohio | 2,631,669 | 2,886,830 | 2,786,460 |
| Missouri | 2,254,926 | 2,435,700 | 2,276,088 |
| New Jersey | 2,001,496 | 2,110,310 | 2,050,593 |
| Massachusetts | 1,670,556 | 1,805,508 | 1,763,989 |
| Other States | 6,589,470 | 7,463,904 | 7,444,287 |
| | 34,462,882 | 37,529,339 | 36,697,634 |

### II. *b*. CONSUMPTION OF MALT LIQUORS IN THE UNITED STATES.

The consumption of malt liquors in the United States is thus estimated by the Bureau of Statistics of the Treasury Department:

| | 1897. | 1898. | 1899. |
|---|---|---|---|
| Domestic, in gallons | 1,066,307,704 | 1,161,769,114 | 1,182,723,202 |
| Imported, " " | 3,002,558 | 2,457,348 | 2,797,427 |
| Total, " " | 1,069,310,262 | 1,164,226,462 | 1,185,520,629 |
| Per capita, " " | 14.69 | 15.64 | 14.94 |

### II. *c*. BEER PRODUCTION AND CONSUMPTION OF THE WORLD FOR 1897 AND 1898.

| | Production in hectolitres. | Consumption per capita. |
|---|---|---|
| Germany | 61,300,000 | 115.8 litres. (Bavaria 235.8 " ) |
| United States (with South American countries) | 55,400,000 | 47.0 " |
| Great Britain | 55,000,000 | 145.0 " |
| Austria-Hungary | 20,610,000 | 44.0 " |
| Belgium | 12,410,000 | 169.2 " |
| France | 8,870,000 | 22.4 " |
| Russia | 4,580,000 | 4.7 " |
| Denmark | 1,980,000 | 85.0 " |
| Switzerland | 1,580,000 | 55.0 " |
| Holland | 1,485,000 | 40.0 " |
| Sweden | 1,450,000 | 11.0 " |
| Norway | 540,000 | 15.3 " |
| Other countries | 1,195,000 | . . |

(Zeitsch. für Angew. Chem., 1899, p. 868.)

### III. *a*. CONSUMPTION OF WINE IN THE UNITED STATES.

The consumption of wine in the United States, according to the Bureau of Statistics of the Treasury Department, has been:

| | 1897. | 1898. | 1899. |
|---|---|---|---|
| Domestic, in gallons | 33,940,319 | 17,453,684 | 22,135,587 |
| Imported, " " | 4,647,988 | 3,113,633 | 3,525,109 |
| Total, " " | 38,588,307 | 20,567,317 | 26,360,696 |
| Per capita, " " | 0.53 | 0.28 | 0.35 |

III. *b.* WINE PRODUCTION OF THE WORLD FOR 1897 AND 1898.

| | 1897. | | 1898. | |
|---|---|---|---|---|
| France | 32,350,700 | hectolitres | 32,282,300 | hectolitres. |
| Algeria and Tunis | 4,457,758 | " | 5,341,000 | " |
| Italy | 25,958,500 | " | 31,500,000 | " |
| Spain | 18,900,000 | " | 24,750,000 | " |
| Portugal | 2,500,000 | " | 2,100,000 | " |
| Austria-Hungary | 3,000,000 | " | 2,800,000 | " |
| Russia | 2,500,000 | " | 3,120,000 | " |
| Switzerland | 1,250,000 | " | 1,160,000 | " |
| Germany | 2,775,576 | " | 1,406,818 | " |
| Roumania | 3,200,000 | " | 3,900,000 | " |
| United States | 1,147,000 | " | 1,300,000 | " |
| Other countries | 10,261,000 | " | 9,975,700 | " |
| | 108,300,534 | " | 119,635,818 | " |

IV. *a.* PRODUCTION OF DISTILLED SPIRITS IN THE UNITED STATES.

| Variety of Spirit. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| | Gallons. | Gallons. | Gallons. | Gallons. |
| Bourbon whiskey | 16,935,862 | 6,113,726 | 13,439,459 | 17,256,331 |
| Rye whiskey | 9,153,066 | 4,269,220 | 8,818,240 | 10,792,565 |
| Alcohol | 9,960,301 | 9,503,353 | 11,672,795 | 11,974,354 |
| Rum | 1,490,228 | 1,294,157 | 1,340,547 | 1,494,379 |
| Gin | 1,098,376 | 1,159,314 | 1,267,579 | 1,266,823 |
| "High wines" | 198,299 | 206,739 | 174,124 | 420,833 |
| "Neutral or cologne spirit" | 25,564,738 | 16,877,306 | 20,613,205 | 25,876,229 |
| Miscellaneous spirits | 22,187,833 | 23,041,833 | 23,436,264 | 27,983,051 |
| Fruit brandy | 3,403,852 | 1,813,427 | 2,906,198 | 3,097,769 |
| Total | 89,992,555 | 64,279,075 | 83,668,411 | 100,162,334 |

IV. *b.* CONSUMPTION OF DISTILLED SPIRITS IN THE UNITED STATES.

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| | Proof gallons. | Proof gallons. | Proof gallons. | Proof gallons. |
| Domestic spirits from fruit | 1,440,810 | 1,146,131 | 1,411,448 | 1,306,218 |
| All other domestic spirits | 68,069,563 | 69,789,991 | 79,159,590 | 84,614,652 |
| Imported for consumption | 1,541,504 | 2,230,711 | 916,549 | 1,389,358 |
| Total | 71,051,877 | 73,166,833 | 81,487,587 | 87,310,228 |
| Per capita | 1.00 | 1.01 | 1.10 | 1.15 |

IV. *c.* PRODUCTION OF DIFFERENT COUNTRIES, CALCULATED ON A BASIS OF PURE ALCOHOL (100 PER CENT.) IN HECTOLITRES.

| Countries. | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Germany | .... | 3,333,648 | 3,100,505 | 3,287,890 | .... |
| Austria | 1,368,494 | 1,397,780 | .... | .... | .... |
| Hungary | 942,460 | 984,301 | .... | .... | .... |
| Spain | 420,000 | 302,000 | .... | .... | .... |
| Sweden | .... | .... | 179,870 | 184,762 | .... |
| France | .... | .... | 2,028,022 | 2,263,744 | 2,533,925 |
| Holland | 336,000 | 337,500 | 343,000 | .... | .... |
| Belgium | .... | .... | .... | 296,551 | .... |

# CHAPTER VII.

## MILK INDUSTRIES.

### I. Raw Materials.

MILK is the fluid secreted by the females of the mammalia for the nourishment of their young, and is therefore a food specially adapted for the needs of the animal organism at this stage, furnishing all the nutrients required and furnishing them in the proper proportion. As will be seen from its analysis, it occupies an intermediate position between the cereal and the strictly animal foods, approximating, of course, more nearly the latter, but showing in one important constituent, milk-sugar, its relationship to the former.

Milk is a secretion of the mammary glands, in which it is produced proximately by certain processes of diffusion from the blood and immediately by the breaking down of the gland-cells themselves, so that milk is described as cell-material liquefied. The milk of all mammalia is essentially the same in its constituents, although these vary somewhat in their relative proportions.

The essential constituents of milk are water, fat, casein, albumen, milk-sugar, and salts. The relative proportion of these constituents in the milk of different animals may be seen from the following table of analyses from Wynter Blyth: *

| | Fat. | Casein. | Albumen. | Milk-sugar. | Ash. | Total solids. | Water. |
|---|---|---|---|---|---|---|---|
| Human milk | 2.90 | 2.40 | 0.57 | 5.87 | 0.16 | 12.00 | 88.00 |
| Cow's milk | 3.50 | 3.98 | 0.77 | 4.00 | 0.17 | 13.13 | 86.87 |
| Camel's milk | 2.90 | 3.84 | | 5.66 | 0.66 | 13.06 | 86.94 |
| Goat's milk | 4.20 | 3.00 | 0.62 | 4.00 | 0.56 | 12.46 | 87.54 |
| Ass's milk | 1 02 | 1.09 | 0.70 | 5.50 | 0.42 | 8.83 | 91.17 |
| Mare's milk | 2.50 | 2.19 | 0.42 | 5.50 | 0.50 | 11.20 | 88.80 |
| Sheep's milk | 5.30 | 6.10 | 1.00 | 4.20 | 1.00 | 17.73 | 82.27 |

In taking up milk as a raw material for industrial utilization, we shall refer to cow's milk exclusively unless otherwise specified.

The fat exists in the milk in the form of minute globules suspended in a thin liquid, forming for the time a perfect emulsion with the aqueous solution of the other constituents. The fat is essentially an intimate mixture of the glycerides of the fatty acids, palmitic, stearic, and oleic, not soluble in water, and of the glycerides of certain soluble volatile fatty acids, such as butyric, caproic, caprylic, and capric.

The casein of milk exists apparently in the fresh milk as a soluble com-

* Foods, Composition and Analysis, 1882, pp. 214, etc.

pound of albumen and calcium phosphate, which by the action of rennet (a ferment from the calf's stomach) is converted into the insoluble one known as casein. The casein precipitated by rennet contains five to eight per cent. of ash, consisting almost entirely of calcium phosphate. If, however, this calcium phosphate compound of albumen is decomposed by mineral acids or acetic acid, the casein precipitated contains only traces of ash. Lactic acid gives the same result, so that the casein coagulated by the souring of the milk shows less ash than that precipitated by rennet from sweet milk. On the other hand, carbon dioxide will act like rennet. The soluble compound existing in the fresh milk is considered to be that of the tricalcium phosphate with albumen, while the insoluble one precipitated by rennet is the acid calcium phosphate with albumen. Pure casein is a perfectly white brittle crumbling substance, insoluble in water, but soluble in very dilute acids or very dilute alkalies. In the action of rennet and acids upon casein a portion is apparently altered into what are called peptones (*lacto-protein* or *lacto-peptone*) and remains dissolved in the whey of the milk. The albumen (or soluble nitrogenous matter) of milk seems to be analogous to the albumen of blood. It may be obtained by precipitation with basic acetate of lead or by dialysis as a yellowish flaky mass. The proportion of albumen in milk is always, according to Wynter Blyth, about one-fifth of the casein.

Two additional nitrogenous compounds have been found by Blyth to exist in small amounts in milk, to which the names *galactine* and *lacto-chrome* have been given.

Milk-sugar, which is an important and characteristic constituent of the milk, is obtained from the serum, or "whey." After the separation of the curd has been effected by the addition of rennet the whey is evaporated on the water-bath, and yields the milk-sugar in hard crystals. These when purified by animal charcoal and recrystallized show the composition $C_{12}H_{22}O_{11} + H_2O$. It is easily distinguished from other sugars of the same formula. It is converted by boiling with dilute acids into dextrose and galactose, which latter has one-fifth less copper-reducing power than dextrose. It undergoes the lactic fermentation readily but the alcoholic with some difficulty.

The ash of milk consists of calcium citrate and the phosphates and chlorides of potassium, sodium, calcium, and magnesium, the salts that are specially needed for the growth of the bone-material in the young nourished by the milk.

Cow's milk is a white or yellowish-white liquid, nearly opaque, except in very thin layers, when it has a bluish opalescent appearance, and a specific gravity of from 1.029 to 1.035. It has a mild sweetish taste and a slight but characteristic odor, stronger when still warm from the cow. Upon allowing milk to remain at rest for some time it undergoes two changes: First, a yellowish-white layer forms on the surface known as "cream," due to the rising of the specifically lighter fat-globules from the body of the liquid where they were held back in emulsion with the aqueous liquid; and, second, the aqueous liquid after a time undergoes further separation into a thick coagulum or "curd" of casein and a thinner liquid or "whey," holding the sugar of milk, any lactic acid formed from it, and the salts in solution. Both of the changes are of the greatest importance, as upon them are based the great milk industries, butter-making and cheese-making respectively.

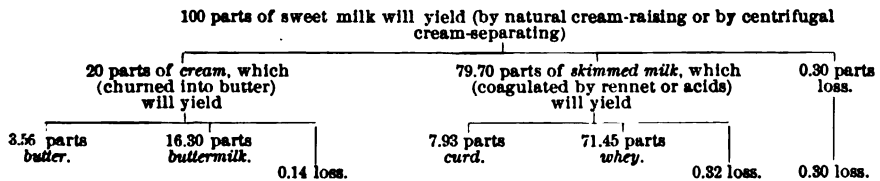
The rising of the cream is largely dependent ordinarily upon two conditions: First, the temperature,—a low temperature being favorable to the

separation; and, second, complete freedom from agitation. These conditions are not, however, indispensable, as will be seen later (see p. 255) in speaking of the use of centrifugals for the separation of cream.

The rising of the cream is generally allowed to be an entirely spontaneous change on the part of the milk and the first one which it undergoes, but in some creameries a little sour milk (containing lactic acid) is added to the fresh milk, when first put in the cream-rising pans, so that the curdling of the casein may facilitate the escape of the fat-globules and the rising of the cream. In such a case what remains on removal of the cream is not ordinary skimmed milk, but a sour curdled milk. The second change mentioned, that of curdling, is really preceded by a change of some of the milk-sugar into lactic acid (due to lactic fermentation, which sets in very quickly in hot weather or if the milk has not been kept in clean vessels). This souring of the milk may be retarded by the addition of a little carbonate of soda or boric acid. The lactic acid as soon as liberated decomposes the soluble casein compound, before referred to (see p. 252), and the casein is thrown out or coagulated as "curd." The separation of the curd is aided by heat. The liquor in which this coagulated casein floats, the serum of milk, or "whey," contains about one-fourth of the nitrogenous matter of the milk, all of its sugar, and most of its mineral matter. The whey is "sour whey" in case lactic acid has formed as the antecedent of the coagulation, or "sweet whey" in case the casein is thrown out by the action of rennet without the formation of lactic acid.

The composition of the several parts into which the milk is divided by these changes is thus given by Fleischmann:

| | Water. | Fat. | Casein. | Albumen. | Milk-sugar. | Ash. |
|---|---|---|---|---|---|---|
| Whole milk | 87.60 | 3.98 | 3.02 | 0.40 | 4.30 | 0.70 |
| Cream | 77.30 | 15.45 | 3.20 | 0.20 | 3.15 | 0.70 |
| Skim-milk | 90.34 | 1.00 | 2.87 | 0.45 | 4.63 | 0.71 |
| Butter | 14.89 | 82.02 | 1.97 | 0.28 | 0.28 | 0.56 |
| Buttermilk | 91.00 | 0.80 | 3.50 | 0.20 | 3.80 | 0.70 |
| Curd | 59.30 | 6.43 | 24.22 | 3.53 | 5.01 | 1.51 |
| Whey | 94.00 | 0.35 | 0.40 | 0.40 | 4.55 | 0.60 |

And the relative yield of these several constituents from one hundred parts of milk is thus given by the same author:

## II. Processes of Manufacture.

1. MANUFACTURE OF CONDENSED AND PRESERVED MILK.—Condensed milk is milk from which a large portion of the water originally present has been driven off, increasing, of course, in a proportionate degree the percentage of the other constituents. This condensed product may or may not have cane-sugar added to it as a preservative. That to be pre-

served with cane-sugar is made much more concentrated, and is that which is manufactured for export and preservation in sealed tin cans. In its preparation, the milk is first heated to 65.6° to 80° C. (150° to 175° F.) by placing the cans containing the milk in hot water, and is then strained and conveyed to the evaporating vessels, which are usually vacuum-pans. Refined sugar is added during the boiling to the amount of one to one and a half pounds for every quart of the condensed milk produced. The product is drawn off into cans, cooled to about 70° F., and then weighed into tins, which are at once soldered down.

Condensed milk free from cane-sugar is only concentrated to about one-half the degree attained in the other product, and is then cooled and filled into stone or glass flasks provided with ordinary air-tight stoppers. It will remain fresh for from one to two weeks, and requires only to be diluted with its own bulk of water in order to yield the counterpart of the original milk.

Preserved milk is either prepared by Appert's process, which consists in boiling the milk to destroy ferments and keeping it then in hermetically-sealed vessels, or by Scherff's improved process, whereby the milk is filled into glass bottles which are stopped with corks previously steamed and then fastened in by clamps, and then heated in closed boilers under a pressure of from two to four atmospheres to about 120° C. The bottles are then taken out of the pressure-vessel and cooled down, with the corks covered with flannel soaked in paraffine, so that as they cool the air entering through the pores of the corks shall be filtered. When cooled down, the cork, which has been drawn into the neck of the bottle considerably, is covered with a layer of paraffine. This kind of preserved milk is used largely in Germany for invalids and children.

2. Of Butter.—The first operation in this connection is the separation as completely as possible of the cream from the rest of the milk. This is generally a spontaneous process, it is true, but its completeness is dependent largely upon the conditions before referred to. There are various ways in which the raising of the cream is allowed to take place. We may mention the Holstein process, in which the fresh milk is at once set to raise cream in wide shallow pans at a temperature of 12° to 15° C. (53.6° to 59° F.), the Dutch process, in which it is first rapidly cooled down in large vessels immersed in cold water to about 15° C. (59° F.) and then transferred to the shallow pans for the raising of the cream, and the Schwartz process, largely used in Northern Europe, which differs from the Dutch process chiefly in using much deeper pans at a lower temperature, 4.4° to 10° C. (40° to 50° F.). Very similar to this last mentioned are the Hardin and the Cooley methods, which also use deep cream-raising pans. In the former of these, ice and not ice-water is used to effect the cooling, the pans being exposed to the influence of air cooled by ice, the claim being made that the cream is obtained in more solid condition. In the Cooley method, used largely in this country, the water not only surrounds the can outside as high as the milk inside, but is made to rise an inch or two above the lid, so that the can is completely submerged and all contamination from external sources prevented.

The processes which use shallow pans give a larger yield of cream but take a longer time (thirty-six to forty-eight hours as against eighteen to twenty-four for those using deep pans). Within the last ten years the principle of the centrifugal has been applied to the separation of the cream

from the milk, and this has proven itself so successful that in most large creameries it is now utilized. The milk is placed in a horizontal rotating vessel driven at a high rate of speed, which causes the heavier milk fluid to gravitate towards the circumference of the vessel, whilst the cream remains nearer the centre and rises towards the upper part of the rotating bowl, whence it is removed by a conveniently-placed aperture on the side of the vessel. An exit is also provided for the gradual removal of the skimmed milk, thus making room for fresh milk to be added to the apparatus and allowing the process to be carried on continuously. Figs. 74 and 75 show the Laval cream separator in general view and in section. The fresh milk is admitted through a funnel, the tube of which is prolonged so as to deliver the milk near the bottom of the revolving drum. The skim-milk flows out through an opening, *t*, and the cream through a higher opening, the relative position of which can be changed by an adjustable screw above. The cream obtained by these centrifugal separators seems to be freer from mechanically-enclosed casein than that gotten in any of the old separation processes, as is seen in the appended cream analyses by Bell,* where samples 2 and 6 were separated by the centrifugal separator:

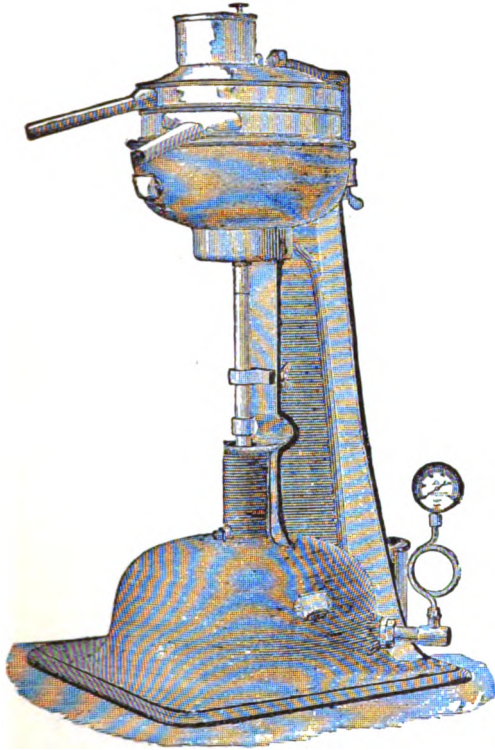
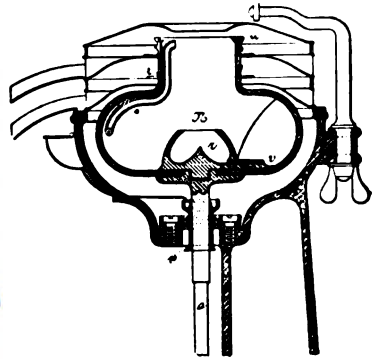



Fig. 74.

Fig. 75.

| | | Water. | Fat. | Milk-sugar. | Casein. | Ash. |
|---|---|---|---|---|---|---|
| 1. | Raw cream | 54.02 | 39.40 | 1.85 | 3.76 | 0.57 |
| 2. | Raw cream | 60.66 | 33.60 | 2.43 | 2.90 | 0.41 |
| 3. | Raw cream | 67.93 | 24.44 | 2.96 | 4.04 | 0.63 |
| 4. | Raw cream | 58.07 | 35.67 | 2.20 | 3.55 | 0.51 |
| 5. | Raw cream | 63.07 | 30.74 | 2.61 | 3.04 | 0.54 |
| 6. | Thick cream | 37.62 | 58.77 | 1.46 | 1.83 | 0.32 |
| 7. | Devonshire clotted cream | 33.76 | 59.79 | 1.01 | 4.97 | 0.47 |

* Analysis and Adulteration of Food, p. 35.

The composition of the skimmed milk of course varies according to the extent to which the cream has been removed. The following analyses by Voelcker represent its average composition as obtained in the ordinary way and as obtained by the Laval separator:

| | Water. | Butter-fat. | Casein. | Milk-sugar. | Ash. |
|---|---|---|---|---|---|
| Ordinary skimmed milk . . . . . . . . . . . . | 89.25 | 1.12 | 3.69 | 5.17 | 0.78 |
| Skimmed milk by Laval separator . . . . . . . . | 90.82 | 0.31 | 3.31 | 4.77 | 0.79 |

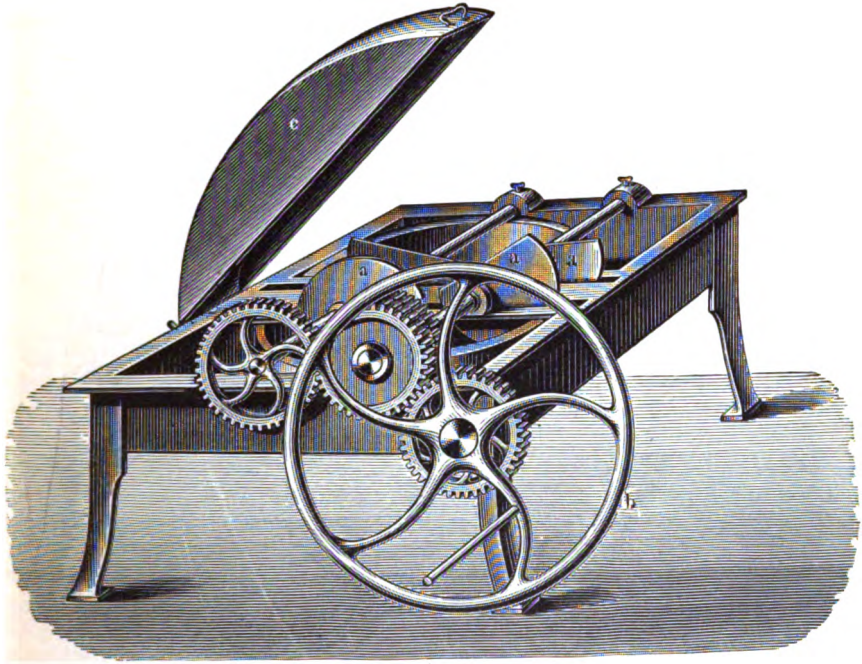
The coalescence of the fat-globules separated in the cream layer is now to be effected to form the compact butter. This is almost universally accomplished by mechanical agitation in the process called churning. The churns may be of very diverse construction, either for hand or power. The cream may be taken as "sweet cream" freshly separated in the centrifugal or raised from deep pans where the skim-milk is still sweet, or it may be "sour cream," which has stood longer and has separated slowly in shallow pans. The sour cream is more easily churned, but the butter will contain more casein, while sweet cream yields a butter with pleasanter taste and better keeping qualities because containing less casein. The temperature most favorable for churning is about 15.5° C. (60° F.). Sometimes cream is heated to a much higher temperature first, and then cooled down to 60° F. before being churned. Butter thus made keeps well.

Butter has almost invariably some salt added to it even when for immediate consumption; the quantity in this case need not be large (five-tenths to two per cent.), but when it is to be packed for preservation or for export considerably more is added, so that it is known as "salt butter." Export butter has also a small addition of sugar, and sometimes saltpetre, added, as well as salt, to preserve it. Genuine butter will always have a yellowish color, which, however, becomes deeper in summer when the cows have an abundance of fresh pasture. Most butter manufacturers now add a little vegetable coloring matter like annato, carrot-color, or saffron, to give the butter this desired yellow tint in winter, when the butter would otherwise be very much lighter in color. All butter will in time become rancid and take a strong disagreeable odor. This is due to the gradual spontaneous decomposition of the butyric ether under the influence of air and light whereby free butyric acid is liberated.

The composition of butter will be more fully spoken of later on in discussing the products of these industries.

3. Of Artificial Butter (*Butterine*, *Oleomargarine*).—The manufacture of substitutes for normal dairy butter began with the experiments of the Frenchman Mège-Mouries in 1870. He found that carefully-washed beef-suet furnished a basis for the manufacture of an excellent substitute for natural butter. The thoroughly-washed and finely-chopped suet was rendered in a steam-heated tank, taking for one thousand parts of fat, three hundred parts of water, one part of carbonate of potash, and two stomachs of pigs or sheep. The temperature of the mixture was raised to 45° C. After two hours, under the influence of the pepsin in the stomachs, the membranes are dissolved and the fat melted and risen to the top of the mixture. After adding a little salt, the melted fat is drawn off,

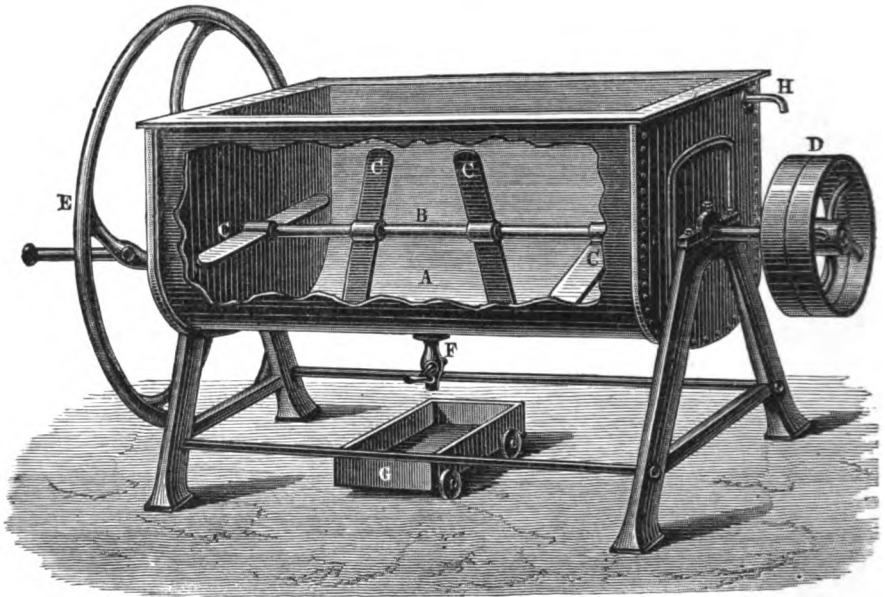
stood to cool so as to allow the stearin and palmitin to crystalline out, and then pressed in bags in a hydraulic press. Forty to fifty per cent. of solid stearin remains, while fifty to sixty per cent. of fluid oleopalmitin (so-called "oleomargarine") is pressed out. Mège then mixed the "oleo oil" with ten per cent. of its weight of milk and a little butter-color and churned it. The fat-cutting process of Mège-Mouries is shown in Fig. 76

FIG. 76.

and the churning of the "oleo oil" in Fig. 77. The product was then worked, salted, and constituted the "oleomargarine," or butter substitute. Various improvements have been made in the process of Mège, and it has been found that leaf-lard can be worked in the same way as beef-suet, and will yield an oleopalmitin suitable for churning up into a butter substitute.

The processes now followed are given substantially as described by Mr. Phil. D. Armour in his testimony before a committee of Congress:* "The fat is taken from the cattle in the process of slaughtering, and after thorough washing is placed in clean water and surrounded with ice, where it is allowed to remain until all animal heat has been removed. It is then cut into small pieces by machinery and cooked at a temperature of about 150° F. (65.6° C.) until the fat in liquid form has separated from the fibrin or tissue, then settled until it is perfectly clear. Then it is drawn into graining-vats and allowed to stand for a day, when it is ready for the presses. The pressing extracts the stearin, leaving a product commercially known as 'oleo oil,' which when churned with cream or milk, or both, and with usually a proportion of creamery butter, the whole being properly salted, gives the new

* Department of Agriculture, Bulletin No. 13, Part i. p. 16.

food product, oleomargarine. In making butterine we use 'neutral lard,' which is made from selected leaf-lard in a very similar manner to oleo oil, excepting that no stearin is extracted. This neutral lard is cured in salt brine for forty-eight to seventy hours at an ice-water temperature. It is

Fig. 77.

then taken and with the desired proportion of oleo oil and fine butter is churned with cream and milk, producing an article which when properly salted and packed is ready for the market.

"In both cases coloring matter is used, which is the same as that used by dairymen to color their butter. At certain seasons of the year—viz., in cold weather—a small quantity of sesame oil or salad oil made from cotton-seed oil is used to soften the texture of the product."

It will be seen that in this process a higher temperature is used in rendering the fat than was used originally by Mège. He obtained about fifty per cent. of oleo oil. The manufacturers now obtain sixty-two per cent. or more. The oleo oil from beef-suet and the neutral lard from leaf-lard are frequently mixed, the proportions varying according to the destination of the product; a warm climate calling for more "oleo," a cold one for more "neutral." In ordinary practice about forty-eight gallons of milk are used for churning with the oil per two thousand pounds of product. Plain oleomargarine is the cheapest product made. By adding to the material in the agitator or churn more or less pure butter what is known as butterine is produced, two grades of which are commonly sold,—viz., "creamery butterine," containing more, and "dairy butterine," containing less, butter.

Large quantities of oleo oil are now manufactured and exported as such from the United States to Europe, notably to Holland, where it is made up into oleomargarine butter. There are said to be seventy manufactories of this kind in Holland which work up oleo oil from all parts of the world.

4. Cheese-making.—The manufacture of cheese depends upon the

property possessed by casein of being curdled by acids or ferments. In the case of sour milk, the milk-sugar has developed by the lactic fermentation some lactic acid, and this, as before stated, promptly throws out the casein in the insoluble form. In the case of sweet milk we usually accomplish the curdling of the casein not by the use of an acid, but with a ferment contained in the preparation called rennet. This is prepared from the fourth stomach of the calf by first cleansing the stomach, cutting and drying it, and then leaving some brine in contact with its lining membrane for a few days. The salt liquid will thus acquire very active properties, so that a small quantity will curdle a large quantity of milk. We would have then, according as one or the other method is followed, a sour-milk cheese or a sweet-milk cheese. The former have a very minor value commercially, being made mainly for immediate domestic consumption. The latter class include all the more valuable commercial varieties. Of these we may distinguish fat, half-fat (or medium), and lean cheeses, or as they are also designated to indicate their origin, cream cheeses, whole milk cheeses, and skim-milk cheeses. As these last names indicate, the material may differ. We may have, moreover, all gradations or mixtures of cream, whole milk, and skim-milk used for the various grades manufactured.

In cheese-making from sweet milk, the milk, whether whole, mixed with cream, or skimmed, is heated to about 30° C. (86° F.) and the rennet added. It curdles usually in from thirty to forty minutes. After the curd has formed and been cut, or "broken down," the heat is raised to 98° F. (36° C.) to insure the souring of the whey and its more complete separation from the curd. Or the curd produced at not over 86° F. (30° C.) is after being cut collected in a heap, covered with a cloth to preserve the heat, and allowed to stand an hour to develop the acidity which serves to harden the curd and promote its separation from the whey. The curd is now cut up, worked to free it from the whey, salted and pressed. After it has acquired sufficient coherence (which requires from twelve to fourteen hours) it is taken from the press and placed in the curing-room to "ripen." This ripening process is essentially a fermentative one, and during its progress the curd loses its insipidity and acquires the characteristic taste and flavor of cheese.

In this process of ripening, the milk-sugar remaining in the cheese becomes transformed partly into lactic acid and partly into alcohol and carbon dioxide. In some varieties the carbon dioxide swells up ("huffs") the cheese-mass and gives it the porous character so noticeable in the ripened cheese.

Fresh cheese has an acid reaction, but this diminishes more and more in the ripening, as the casein is gradually altered, soluble albuminoids, peptone-like bodies, and organic bases like leucine, tyrosine, and amines being formed.

Some cheeses, especially the cream cheeses, are not pressed, but come on the market as soft cheeses. In these the curdling by rennet has also been effected at a lower temperature than in the case of the hard cheeses.

Cheese has also been manufactured extensively in this country from skimmed milk to which oleomargarine or "oleo oil" has been added so as to give the finished product the character of a whole-milk cheese. This product is now quite supplanted, however, by the "lard cheese," which, according to Caldwell,* was made in 1882 at over twenty factories in the State of New York. In this process an emulsion of lard is made by bringing

* Second Annual Report New York State Board of Health, p. 529.

together in a "disintegrator" lard and skimmed milk both previously heated to 140° F. in steam-jacketed tanks; the "disintegrator" consists of a cylinder revolving within a cylindrical shell: the surface of the cylinder is covered with fine serrated projections, each one of which is a tooth with a sharp point; as this cylinder revolves rapidly within its shell the mixture of melted lard and hot skimmed milk is forced up into the narrow interspace; and the lard becomes very finely divided and most intimately mixed, or "emulsionized," with the milk. This emulsion consists of from two to three parts of milk to one of lard. In making the cheese, a quantity of this emulsion, containing about eighty pounds of lard, is added to six thousand pounds of skimmed milk and about six hundred pounds of buttermilk in the cheese-vat, and the lard that does not remain incorporated with the milk or curd, usually about ten pounds, is carefully skimmed off. These quantities of the materials yield from five hundred to six hundred pounds of cheese containing about seventy pounds of lard, or about fourteen per cent. About one-half of the fat removed as cream in the skimming of the milk is thus replaced by lard. It is claimed that no alkali or antiseptic is used, and that only the best kettle-rendered lard can be employed, because of the injurious effect of any inferior article on the quality of the cheese, and that before even this lard is used it is deodorized by blowing steam under eighty pounds pressure through it for an hour. According to many witnesses the imitation is excellent, for experts have been unable to pick out lard cheeses from a lot of these and full-cream cheeses of good quality together.

## III. Products.

1. Condensed and Preserved Milk.—The distinction between condensed milk prepared with the addition of cane-sugar and that prepared without sugar has already been referred to in speaking of the manufacture of this class of products. The first of these classes forms a white or yellowish-white product of about the consistency of honey and ranging in specific gravity from 1.25 to 1.41. It should be completely soluble in from four to five times its bulk of water without separation of any flocculent residue, and then possess the taste of perfectly fresh sweetened milk.

The second class of condensed milk preparations, those without addition of cane-sugar, are not boiled down to the same degree and remain perfectly liquid, and are put up therefore in glass bottles instead of being sealed in cans. Analyses of both classes are given on the authority of Battershall.*

*Condensed Milk with Addition of Sugar.*

| Brand. | Water. | Fat. | Cane- and milk-sugar. | Casein. | Salts. |
|---|---|---|---|---|---|
| Alderney | 30.05 | 10.08 | 46.01 | 12.04 | 1.82 |
| Anglo-Swiss (American) | 29.46 | 8.11 | 50.41 | 10.22 | 1.80 |
| Anglo-Swiss (English) | 27.80 | 8.24 | 51.07 | 10.80 | 2.09 |
| Anglo-Swiss (Swiss) | 25.51 | 8.51 | 53.27 | 10.71 | 2 00 |
| Eagle | 27.30 | 6.60 | 44.47 | 10.77 | 1.86 |
| Crown | 29.44 | 9.27 | 49.26 | 10.11 | 1.92 |

* Food Adulteration and its Detection, p. 53.

*Condensed Milk without Cane-sugar.*

| Brand. | Water. | Fat. | Milk-sugar. | Casein. | Salts. |
|---|---|---|---|---|---|
| American | 52.07 | 15.06 | 16.97 | 14.26 | 2.80 |
| New York | 56.71 | 14.13 | 13.98 | 13.18 | 2.00 |
| Granulated Milk Company | 55.43 | 13.16 | 14.84 | 14.04 | 2.53 |
| Eagle | 56.01 | 14.02 | 14.06 | 13.90 | 2.01 |

2. Butter and Butter Substitutes.—Commercial butter is more or less granular, and the more perfect the granular condition the higher is its quality considered. Special effort has been made in the case of oleomargarine or butterine to imitate this granulation, as the artificial product does not naturally tend to show such appearance. A good butter when fresh has a pleasant fragrant odor and agreeable taste, but the flavor, like the color, varies with the food of the cow, certain plants, like garlic, giving a quite pronounced flavor to both milk and butter. At ordinary temperatures butter is easily cut or moulded, and it readily melts to a transparent, light-colored oil. It always contains, according to the thoroughness with which it has been kneaded and washed, more or less casein, which is very liable to undergo decomposition, and hence the necessity for the addition of larger or smaller amounts of salt, which acts as a preservative. When the butter-fat is freed from curd and water by melting the butter and drawing off the oily layer it may be kept for a long time without change.

This butter-fat is made up, as was stated in speaking of the fat of milk, of the glycerides of oleic, palmitic, and stearic acids (the so-called insoluble acids) and the glycerides of butyric, caproic, caprylic, and capric acids (the so-called soluble acids). The proportion in which they exist in butter-fat varies within very slight limits only, so that five to six per cent. may be called the average percentage of the soluble acids, and eighty-eight per cent. the average percentage of the insoluble acids present in butter-fat. This gives a very important means of distinguishing between a natural butter and oleomargarine or natural butter adulterated with the imitations. In such butter the glycerides of the soluble acids (butyric, etc.) are either wanting entirely or, if a little cream was used in the churning with "oleo oil" present, in very much smaller amount than the normal. This distinction will be evident from the analyses of normal butter and oleomargarine butters, given on the authority of Dr. Bell.*

*Genuine Butter, showing Range of Variation in Composition of the Fat.*

| | Water. | Salt. | Curd. | Butter-fat. | Specific gravity at 100° F. | Percentage of fixed acids in fat. | Percentage of soluble acids as butyric. | Melting point, Fahrenheit. |
|---|---|---|---|---|---|---|---|---|
| 1. . . | 7.55 | 1.03 | 1.15 | 90.27 | 913.89 | 85.56 | 7.41 | 85° F. |
| 2. . . | 11.71 | 3.60 | 0.95 | 83.74 | 911.45 | 88.24 | 5.41 | 90° F. |
| 3. . . | 11.42 | 1.29 | 1.12 | 86.17 | 910.47 | 88.53 | 4.84 | 90° F. |
| 4. . . | 12 55 | 0 89 | 0.74 | 85.82 | 910.20 | 89.00 | 4.57 | 90° F. |
| 5. . . | 14.62 | 1.48 | 1.88 | 82.02 | 910.70 | 89.00 | 4.50 | 91° F. |

* Analysis and Adulteration of Foods, pp. 68 and 70.

*Analyses of Oleomargarine Butter or Butterine.*

| Water. | Salt. | Curd. | Fat. | Specific gravity at 100° F. | Percentage of fixed acids. | Percentage of soluble acids. | Melting point. Fahrenheit. |
|---|---|---|---|---|---|---|---|
| 14.30 | 3.81 | 0.48 | 81.41 | 903.84 | 94.34 | . . | 82° F. |
| 11.21 | 1.70 | 1.73 | 85.36 | 902.34 | 94.83 | 0.66 | 78° F. |
| 12.33 | 4 00 | 1.09 | 82.58 | 903.15 | 95.04 | 0.47 | 79° F. |
| 5.32 | 1.09 | 0.67 | 92 92 | 903.79 | 96 29 | 0.23 | 81° F. |
| 13.21 | 3.99 | 1.07 | 81.73 | 901.36 | 95.60 | 0.16 | 78° F. |

The best grades of artificial butter do not differ in appearance from ordinary butter. To induce the proper granulation of the oleomargarine, it is chilled thoroughly with fragments of ice immediately after it is taken from the churn and before kneading or salting it. In color, consistence, and taste it may be made to imitate the natural butter so as to deceive most persons. A distinction, it is said, however, can always be noted in the taste when it is melted upon hot boiled potatoes, to which it imparts a peculiar taste recognizable as distinct from that of a true butter.

3. CHEESE.—The general classification of the cheeses has been given in speaking of the methods of manufacture, and the distinction between the fat and lean cheeses, between cream cheese, whole-milk and skimmed-milk cheeses given. The terms hard and soft cheeses are applied according as the curd has or has not been pressed in the process of manufacturing. Most of the names which have been attached to the different varieties of cheese are those of localities. We will indicate the character of a few of these.

Neufchâtel cheese is a Swiss cream cheese.

Limburger cheese is a soft fat cheese.

Fromage de Brie is a soft French cheese rapidly ripening and developing ammoniacal compounds.

Camembert cheese is also a cream cheese.

Roquefort cheese is a cheese made from the milk of the ewe.

Gruyère cheese is a peculiarly flavored Swiss cheese.

Cheddar cheese is a hard cheese made with whole milk.

Single and double Gloucester are made, the first from a mixture of skimmed and entire milk, and the second from the entire milk.

Parmesan cheese is a very dry cheese, with a large amount of casein and only a moderate percentage of fat.

Eidam cheese is a Dutch cheese, also relatively dry, and covered with red coloring.

In illustration of the chemical composition of these different varieties of cheese we will append three tables, the first of analyses from miscellaneous sources, and the second and third from Bell,* giving a fuller study of the composition of the cheeses and showing the difference between the fat normally belonging to the cheese and the fat added in the shape of lard or "oleo oil" in adulterated cheeses.

* Analysis and Adulteration of Foods, pp. 79 and 82.

| | Water. | Fat. | Casein. | Non-nitrogenous and loss. | Ash. |
|---|---|---|---|---|---|
| Neufchâtel (Fleischmann) | 34.50 | 41.90 | 13.00 | 7.00 | 3.60 |
| Emmenthaler (Fleischmann) | 36.10 | 29.50 | 28.00 | 3.30 | 3.10 |
| Limburger (Fleischmann) | 35.70 | 34.20 | 24 20 | 3.00 | 2.90 |
| Brie (Wynter Blyth) | 51.87 | 24.83 | 18.30 | . . | 5.00 |
| Camembert (Wynter Blyth) | 51.30 | 21.50 | 19.00 | 3.50 | 4.70 |
| Parmesan (Wynter Blyth) | 27.56 | 15.95 | 44.08 | 6.69 | 5.72 |

| | 100 Parts contain | | | | | Proportion of fat in 100 parts of dry cheese. | Proportion of fat in 100 parts of casein and fat. | Salt percentage in cheese. | Percentage Composition of the Fat. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Water. | Fat. | Casein. | Free acid as lactic. | Ash. | | | | Soluble acid. | Insoluble acid. |
| Stilton | 23.57 | 39.13 | 32.55 | 1.24 | 3.51 | 51 19 | 52.50 | 0.67 | 4.42 | 88.96 |
| American (red) | 28.63 | 38.24 | 29.64 | . | 3.49 | 53.57 | 54.12 | 0.72 | 4.26 | 89.06 |
| American (pale) | 31.55 | 35.93 | 28.83 | 0.27 | 3.42 | 52.49 | 53.34 | 0.82 | 4.81 | 88.49 |
| Roquefort | 32.26 | 34.38 | 27.16 | 1.32 | 4.88 | 50.75 | 54.24 | 3.04 | 4.91 | 88.70 |
| Gorgonzola | 31.85 | 34.34 | 27.88 | 1.35 | 4.58 | 49.02 | 53.08 | 2.11 | 4.40 | 89.18 |
| Cheddar (medium) | 35.60 | 31.57 | 28.16 | 0.45 | 4.22 | 46.26 | 50.49 | 1.43 | 4.55 | 88 75 |
| Gruyère | 33.66 | 30.69 | 30.67 | 0.27 | 4.71 | 48.78 | 47.02 | 0.81 | 4.41 | 88.97 |
| Cheshire | 37.11 | 30.68 | 26.93 | 0.86 | 4.42 | 48.78 | 50.84 | 1.69 | 5.55 | 87.76 |
| Single Gloucester | 35.75 | 28.35 | 31.10 | 0.31 | 4.49 | 44.12 | 45.24 | 1.28 | 6.68 | 86.89 |
| Dutch (Eidam) | 41.30 | 22.78 | 28.25 | 0.57 | 7.10 | 38.80 | 42.41 | 4.45 | 5.84 | 87.58 |

*Analyses of Oleomargarine and Lard Cheeses.*

| | 100 Parts contain | | | | Per cent. of salt. | 100 Parts of Fat contain | | Melting point of fat. |
|---|---|---|---|---|---|---|---|---|
| | Water. | Fat. | Casein and free acids. | Ash. | | Insoluble acids. | Soluble acids. | |
| Oleomargarine cheese | 30.95 | 28.80 | 36.27 | 3.98 | 1.14 | 92.43 | 2.16 | 77° F. (25° C.). |
| Lard cheese | 31.30 | 24.66 | 38.87 | 5.17 | 1.55 | 92.88 | 1.55 | 92° F. (33.3° C.). |

4. Milk-sugar.—The manufacture of crystallized milk-sugar (lactose) has developed greatly in recent years, and a perfectly white, well-crystallized product is now obtained. For its preparation, the sweet skim-milk as it comes from the cream separator is precipitated with acetic acid, filtered, and boiled either in open steam-heated evaporators or in vacuum pans. This first boiling should take several hours. The whey during the boiling becomes more cloudy, but suddenly clears, and the remaining albuminoids will separate in large flocks that can readily be filtered. It is to be filtered hot and boiled to crystallization in a vacuum pan. The raw sugar so obtained can be refined and made white exactly as described under cane-sugar. As the first crystallization is all that can be brought to satisfactory color and purity, the yield is not much over ten per cent. of the total sugar contained in the milk.

5. Koumiss.—Koumiss is an alcoholic drink made by the fermentation of milk. As made by the fermentation of mare's milk it has long been a favorite beverage with the Tartars and other Asiatic tribes. Cow's milk has been used chiefly in making it in both Europe and America. Mare's milk is the more suitable for fermentation because of the larger percentage of milk-sugar which it contains.

The fermentation is started by mixing fresh milk with some already soured. Both the lactic and the alcohol fermentations are set up, with the production of lactic acid, alcohol, and carbonic acid gas. Some of the albuminoids are also changed into peptones. The composition of the koumiss as prepared from both mare's and cow's milk is shown in the accompanying analyses from various sources:

| | Water. | Milk-sugar. | Lactic acid. | Albuminoids. | Fat. | Alcohol. | Carbon dioxide. | Ash. |
|---|---|---|---|---|---|---|---|---|
| Koumiss from mare's milk (Fleischmann) | 91.53 | 1.25 | 1.01 | 1.91 | 1.27 | 1.85 | 0.88 | 0.29 |
| Koumiss from cow's milk (Fleischmann) | 88.93 | 3.11 | 0 79 | 2.03 | 0 85 | 2.65 | 1.03 | 0.44 |
| Koumiss from mare's milk (König) | 92.47 | 1.24 | 0.91 | 1.97 | 1.26 | 1.84 | 0.95 | . . |
| Koumiss from mare's milk (London, 1884) | 91.87 | 0.79 | 1.04 | 1.91 | 1.19 | 2.86 | . . | . . |
| Koumiss from cow's milk (Wiley) | 89.32 | 4.38 | 0.47 | 2.56 | 2.08 | 0.76 | 0.83 | . . |

6. Kephir.—This is a Caucasian product somewhat similar to koumiss, but prepared from cow's milk in leathern bottles by the aid of a peculiar ferment known as "kephir grains." According to Kern, as quoted by Allen (Commercial Organic Analysis, 2d ed., vol. iv. p. 242), the kephir ferment is an elastic cauliflower-like mass found below the snow line on certain bushes. The fungus consists of bacilli and yeast-cells, each cell containing two round spores, whence the name *Dispora caucasina*. When dried, the kephir fungus forms hard yellowish grains about the size of peas. By soaking these in water and adding them to milk, alcoholic fermentation ensues and the kephir is matured in a few days.

The following figures show the comparative percentage composition of fresh milk, kephir, and koumiss:

| | Fresh Milk. | Kephir. | Koumiss. |
|---|---|---|---|
| Fat | 3.8 | 2.0 | 2.05 |
| Proteids | 4.8 | 3.8 | 1.12 |
| Sugar | 4.1 | 2.0 | 2.20 |
| Lactic acid | Trace. | 0.9 | 1.15 |
| Alcohol | None. | 0.8 | 1.65 |
| Water and salts | 87.3 | 90.49 | 91.83 |

7. Casein Preparations.—Casein is now utilized on a large scale, first, as a basis of food preparations; second, as a fixing agent in calico printing instead of albumen; and third, as a substitute for glue in cements. For the first class of compounds, the casein salts of the alkalies and alkaline earths are used, and are obtained by dissolving casein in the calculated amount of caustic alkali, alkali metal, carbonate or phosphate or milk of lime, and evaporating the solution *in vacuo*. The products are dry white powders. For the second class of compounds, casein is generally dissolved in ammonia, the solution evaporated, and the residue mixed with milk of

lime. *Lactarine* is a commercial preparation of this class used as a fixing agent. A mixture of casein with slaked lime sets to a hard insoluble mass, which is sometimes employed as a cement for earthenware and for similar purposes as a cheap substitute for glue.

In making these casein cements the most important point that is to be noted to insure success is the freeing of the casein from all oily matter. Therefore, when curd is prepared from milk, use only the most carefully skimmed milk quite free from cream. When cheese is used, select the poorest and wash it carefully. The washed and kneaded casein or cheese is thoroughly mixed with quicklime and applied quickly. It then sets very rapidly. Silicate of soda solution and borax are also used instead of quicklime, and form excellent cements with casein. *Käseleim pulver*, a ready-made Swiss preparation, will set when moistened.

8. WHEY.—The aqueous liquid remaining after the separation of the butter-fat and the casein, or curd, is termed the whey. Its more important constituent is milk-sugar, which in sour whey has been changed in part into lactic acid. It also contains soluble nitrogenous constituents, such as milk-albumen and peptonized casein. On account of these constituents it is an easily digestible preparation and one assisting digestion. Hence the use of the "whey treatment" in medical practice for dyspeptics and those suffering from enfeebled digestion. The chief importance, however, of the whey is for the extraction of the milk-sugar, which is largely carried out in Switzerland. Other products of minor and local importance only are "whey butter," "whey alcohol," from which latter "whey champagne" is made, and "whey vinegar." The analysis of the average whey has already been given. (See p. 253.)

## IV. Analytical Tests and Methods.

1. FOR MILK.—The specific gravity of milk is an indication of value, as it varies according to the content of fat, being higher for a skimmed milk than for a whole milk. However, when the cream has been removed, the specific gravity may be reduced to that of normal milk by the addition of water, and then the specific gravity determination taken alone would be fallacious. Hence the detection of the adulteration of milk by addition of water cannot be made with entire accuracy by the lactometer or specific gravity hydrometer in use. The lactometer officially used by milk inspectors in New York and other States indicates specific gravities between 1.000 (the specific gravity of water) and 1.038. A specific gravity of 1.021 (taken as the minimum density of genuine milk) is also marked 100°, while the specific gravity of water (1.000) is called 0°. Hence if the lactometer read 70°, the sample is supposed to contain seventy per cent. pure milk and thirty per cent. water. The average lactometric strength of about twenty thousand samples of milk examined by the New York State Dairy Commissioner in the year 1884 was 110°, equivalent to a specific gravity of 1.0319. Another form of lactometer used abroad is the Quevenne-Müller instrument, which is graduated in absolute specific gravity readings between the limits 1.014 and 1.042, and then the limits of pure milk (1.029 to 1.034) indicated, and degrees of dilution with water also indicated as the specific gravity sinks below this. The degree of adulteration of skimmed milk is also indicated on the instrument in the same way.

The *total solids* form an important element in the examination of milk.

In some States the minimum percentage of total solids allowed in a milk is stated by law. (In Massachusetts thirteen per cent.; in New York and New Jersey twelve per cent.) To determine the *water* and *total solids*, five grams of milk are placed in an accurately weighed flat-bottomed platinum capsule and dried, first on the water-bath and afterwards at 105° C., until constant weight is obtained. Ritthausen proposed coagulating the milk with a few cubic centimetres of absolute alcohol before beginning the drying, but this is said to be unnecessary.

To determine the *ash*, ignite the residue of the total solids just obtained, first over a small flame and finally at a dull red heat. Cover the dish, cool in the desiccator, and weigh.

The *fat* determination may be determined roughly by the "cremometer" of Chevallier, which is a graduated jar in which a sample of fresh milk is stood for from twenty-four to thirty-six hours and then the height of the separated cream layer read off. Remembering, however, that all the fat-globules are never likely to rise and form together in the cream layer, more accurate methods are seen to be necessary. A volumetric method of much greater accuracy is that of the lactobutyrometer of Marchand as improved by Tollens and Schmidt. In this the measured milk sample, to which a few drops of sodium or ammonium hydrate has been added, is agitated with ether, and then alcohol added, and the agitation repeated. On standing the graduated tube in warm water the ethereal layer of fat separates out on top the alcoholic ether, and can be read off and the percentage calculated from tables prepared. An improved form of the lactobutyrometer has been described by Caldwell* and the accuracy of the method established. Another volumetric method based upon the same principle, but more complicated in its details, is that of Soxhlet. In this, the milk made alkaline by caustic potash is shaken with ether, and the ethereal solution of the fat rising to the top of the mixture is separated and its specific gravity determined. Liebermann has also described a third volumetric method, and more recently † Morse, Piggot, and Burton have described what seems to be the most accurate of these methods for the determination of the fat of milk volumetrically. Their method consists in the dehydration of the milk by means of anhydrous copper sulphate; the extraction of the fat by means of low boiling petroleum-ether; the saponification of the butter by means of an excess of a standard solution of potassium hydroxide in alcohol; and the determination of the excess of alkali by means of a solution of hydrochloric acid.

More generally relied upon for absolute accuracy are the gravimetric methods, of which Adams's is generally followed. In this a coil of white blotting-paper (or thick filtering-paper) previously purified with ether and dried is made to soak up the milk to be analyzed from a weighed beaker or pipette. The paper coil is then dried in a hot-air oven and placed in a Soxhlet (see p. 79) or similar fat-extraction apparatus connected with an inverted condenser and the fat extracted by ether or petroleum-ether.

The *albuminoids* are estimated by evaporating a weighed portion of milk to dryness and making a combustion of the residue with soda-lime or by the Kjeldahl method of conversion into ammonia compounds and distillation from an alkaline solution. Professor A. R. Leeds ‡ prefers to deter-

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* Amer. Chem. Journ., vii. p. 243. † Ibid., ix. pp. 108 and 222.
‡ Transactions of the College of Physicians, Philadelphia, 1884, p. 263.

mine the albuminoids jointly with the fat by the precipitation with cupric sulphate after the method of Ritthausen as modified by Gerber.

The estimation of the *milk-sugar* by the polariscope is rendered difficult by the presence in milk of various albuminoids, all of which turn the plane of polarization to the left, and the ordinary means of removing these albuminoids by a solution of basic acetate of lead is far from being perfect. Professor Wiley* after extensive experiments upon this has adopted a method of optical analysis, using acid mercuric nitrate to precipitate the albuminoids. He takes the specific rotatory power of milk-sugar as $(a)_D = 52.5$. For details of his procedure the reader is referred to his publication. Milk-sugar may also be determined either volumetrically or gravimetrically with the aid of Fehling's solution. (See p. 158.) In this case, it is also necessary to remove the albuminoids first, and this is done by Ritthausen's method of precipitation with copper sulphate, all excess of this reagent being removed with caustic potash solution. In calculating the results it will be remembered that the copper reducing power of milk-sugar is 70.5° as compared with dextrose at 100°.

The sugar is probably most accurately determined by extraction from the fat-free residue with weak boiling alcohol, filtering the alcoholic fluid, and evaporating to dryness. This leaves the sugar with some mineral matter. On burning and determining this matter as ash the amount of sugar can be gotten.

2. For Butter.—The *water* in butter is determined by drying five grammes of the butter in a platinum dish at a temperature of 100° C. (212° F.) or slightly higher. The melted butter is stirred from time to time to facilitate the escape of the moisture. The water will have been given off in three to four hours, and it has been found that longer heating sometimes causes the melted fat to gain in weight.

To determine the *salt*, the dried butter just obtained is treated with warm ether or petroleum spirit, and the contents of the platinum dish poured on a weighed filter and washed with ether until all fat is removed. The residue and filter are dried and weighed. The salt is then dissolved out by warm water, and the chlorides in the solution estimated volumetrically by tritration with decinormal silver nitrate, using a few drops of potassium chromate as indicator. The difference between the weight of salt ascertained and the total weight of curd and salt on the weighed filter is regarded as the amount of the *casein*, or *curd*, present. If after washing out the salt the residue on the weighed filter be dried and then weighed, the amount of casein so obtained is a little less than that gotten by difference. This is partly due to the small amount of milk-sugar washed out along with the salt and undetermined, and partly to the slight solvent action of warm water on some of the curd.

The percentage of *fat* may be obtained by evaporating the ether filtrate from the previous determination of salt and curd, but the butter-fat is liable to increase in weight by this treatment, and therefore the *fat* is usually gotten by difference after determining the water, casein, salt, and milk-sugar.

The adulteration of butter and the manufacture on a large scale of butter substitutes makes an examination of the butter-fat one of great importance. This examination may be both qualitative and quantitative. The butter-fat is gotten for examination by melting a sample of butter and, after allow-

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* Department of Agriculture, Bulletin No. 13, Part i. p. 113.

ing the water and curd to settle, pouring the clear fat on to a dry warm ribbed filter and collecting the filtrate.

The specific gravity of the butter-fat may be taken, as first suggested by Bell, in a specific gravity bottle at a temperature of 100° F. (37.7 C.), or, as suggested by Estcourt and endorsed by Allen, with the aid of the Westphal balance (see p. 80) at a temperature of 99° to 100° C. (210° to 212° F.). Bell found by his method that the specific gravity of true butter-fat varied from 909.4 to 914 (water 1000), while butterine showed a specific gravity of 901.4 to 903.8. Allen gives the limit for pure butter-fat tested at 99° C. as 867 to 870, while butterine at the same temperature was 858.5 to 862.5.

The *melting point* of the butter-fat is also generally noted. Bell proposed determining the melting point by first suddenly cooling some melted butter-fat by floating the capsule containing it upon ice-water, and then taking a fragment of the congealed butter upon the loop of a platinum wire. This is then introduced close to the bulb of a thermometer in a beaker of water which is being heated from without. As the water becomes warmed the globule melts and the thermometer is read off. An improvement on the method insuring greater accuracy is recorded in Bulletin of the Department of Agriculture, No. 19, p. 72. The melting point of butter usually ranges between 29.5° C. and 33° C. (85° to 90° F.), while the melting point of butterine is stated to be between 25.5° C. and 28° C. (77.9° to 82.4° F.).

The quantitative examination of the supposed butter-fat may be made by several methods,—viz., the determination of the saponification equivalent by Koettstorfer's method,* the determination of the percentage of insoluble fatty acids present as glycerides by Hehner's method,† and the determination of the volatile fat acids after distillation by Reichert's method.‡ To these most generally received methods may also be added the method of Hübl of iodine saturation as determining the character of fatty acids, and the method of Morse and Burton, which combines the Koettstorfer and the Hehner processes, and determines the saponification equivalent of the soluble and the insoluble fat acids separately.

The term "saponification equivalent" is used to indicate the number of grammes of an oil saponified by one equivalent in grammes of an alkali. Thus, tributyrin (the glyceride of butyric acid) has a saponification equivalent of 100.67, while tristearine (the glyceride of stearic acid) has a saponification equivalent of 296.67. Butter-fat, it will be remembered, is a mixture of the several glycerides of the lower or volatile fatty acids and the higher or non-volatile fatty acids. Its saponification equivalent ranges from 241 to 253, the average being [illegible] butterine has a saponification equivalent ranging from 277 to 294, the [illegible] being 285.5. In Hehner's method, the weighed quantity [illegible] [illegible]ified by alcoholic potash, the soap solution evapor[illegible] [illegible] water, and the fatty acids set free by an [illegible] [illegible] They are now brought upon a weighed filt[illegible] [illegible] no longer acid, and then chilled into [illegible] water. The filter is then transferred [illegible] [illegible] dried at 100° C. until constant [illegible] [illegible] also be determined in this process by

[illegible] Analysis, 2d ed., vol. ii. p. 40.
[illegible] [illegible]ation of Foods, Part ii. p. 56.
[illegible] Analysis, 2d ed., vol. ii. p. 45.

collecting the washings which were obtained with boiling water and making them up to one hundred cubic centimetres and then carefully titrating an aliquot portion with decinormal soda solution. This will give the amount of soluble fat acids plus the excess of standard hydrochloric acid used originally in liberating the fat acids. The amount of this excess can be ascertained by carrying through a blank experiment with alcoholic potash and hydrochloric acid, but without the fat. In the analysis of butter-fat the sum of the insoluble fatty acids and of the soluble fatty acids calculated as butyric acid should always amount to fully ninety-four per cent. of the fat taken. The soluble fatty acids calculated as butyric acid should amount to at least five per cent., any notably smaller proportion being due to adulteration. As an average, eighty-eight per cent. of insoluble and five and a half per cent. of soluble acids should be obtained.

While the true percentage of the volatile fatty acids cannot be easily obtained, the amount of alkali needed to neutralize them after distillation can be determined by Reichert's process. According to this, as improved by Meissl, five grammes of the fused and filtered fat are placed in a flask of about two hundred cubic centimetres contents with about two grammes solid caustic potash and fifty cubic centimetres of seventy per cent. alcohol, saponified on the water-bath and evaporated down until all alcohol is driven off. The thick soap-mass remaining is now dissolved in one hundred cubic centimetres of water, forty cubic centimetres of dilute sulphuric acid added, and, after adding a few fragments of pumice-stone, distilled with the aid of a Liebig condenser. About one hundred and ten cubic centimetres of distillate are collected, which requires about an hour. Filter and collect one hundred cubic centimetres in a graduated flask. Add phenol-phthalein as an indicator, and titrate with decinormal alkali. Increase the result by one-tenth, and reckon the result upon five grammes of the substance. It is found that two and a half grammes of butter-fat, examined by Reichert's method, require about thirteen cubic centimetres of the decinormal alkali, while butterine requires only one cubic centimetre. As the difference between these is twelve cubic centimetres, it may be calculated that there is 8.5 per cent. real butter-fat present in a mixture for every cubic centimetre of alkali required over the one cubic centimetre required for ordinary butterine.

Hübl's method is founded on the fact that the three series of fatty acids (acetic, acrylic, and tetrolic) unite in different proportions with the halogens, like chlorine, bromine, and iodine, to form addition products. The number of grammes of iodine absorbed is calculated to one hundred grammes of fat, and this is Hübl's "iodine number." Thus genuine butter has an iodine number from 30.5 to 43.0, while oleomargarine has from 50.9 to 54.9.

Morse and Burton * saponify the combined fatty acids, liberate the free acids, wash out the soluble portion of the mixture, and then saponify again the soluble and the insoluble acids separately. They thus combine the Koettstorfer and the Hehner processes and get a greater certainty as to the character of the fat mixture. Thus they find that with butter 86.57 per cent. of potassium hydrate is required to neutralize the insoluble acids and 13.17 per cent. to neutralize the soluble acids, while with oleomargarine 95.40 per cent. of potassium hydrate is required for the insoluble acids and 4.57 per cent. for the soluble acids.

* Amer. Chem. Journ., x. p. 322.

Perkins* has devised a similar process, which goes further and distils off the volatile fatty acids from the soluble portion washed out of the fatty acid mixture, thus combining the features of the Reichert process with those of the other two.

The chief coloring matter added to butter are the vegetable dyes annato, carotin, fustic, turmeric, marigold, and saffron, the coal-tar dyes Victoria and Martius yellow, and sometimes chrome-yellow (chromate of lead). The following short scheme of testing will show the nature of the butter-color in most cases:

Dissolve the supposed artificially-colored butter in alcohol and add,—

*a.* Nitric acid : greenish coloration, *saffron.*

*b.* Sugar solution and hydrochloric acid : red coloration, *saffron.*

*c.* Ammonia : brownish coloration, *turmeric.*

*d.* Silver nitrate : blackish coloration, *marigold.*

*e.* Evaporate the alcoholic solution to dryness and add concentrated sulphuric acid : greenish-blue coloration, *annato ;* blue coloration, *saffron.*

*f.* Hydrochloric acid : decolorization, with formation of yellowish crystalline precipitate, *Victoria* or *Martius yellow.*

*g.* Separation of a heavy and insoluble yellow powder : *chrome-yellow.*

3. FOR CHEESE.—The methods employed in cheese analysis are in most respects the same as those employed in the examination of butter. The *fat* is best extracted with light petroleum-ether, as common ether dissolves the free lactic acid as well as the fat. The remaining solids not fat can then be dried and weighed. The fat should be examined by Koettstorfer's saponification equivalent method, as the oleomargarine and lard cheeses may be detected in this way. Genuine cheese-fat, according to Muter,† should not consume less than two hundred and twenty milligrammes of potassium hydrate for each gramme used. If the cheese should give unfavorable indications with Koettstorfer's test, then the soluble and insoluble fatty acids are determined in the fat according to Hehner. The percentage of insoluble fat acids in genuine cheese, according to Muter, averages 88.5, while in oleomargarine cheeses it is from 90.5 to 92 per cent.

The *acidity,* calculated as lactic acid, may be determined by treating the residue from the fat determination with water and titrating the washings with decinormal soda solution. The washed residue then is the non-fatty solids.

The *ash* is determined by ignition of the dried cheese before extraction of the fat.

## V. Bibliography and Statistics.

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## STATISTICS.

In the absence of any governmental control of the milk industries no statistics of production representing the entire country can be given except for oleomargarine.

For butter and cheese consumption accurate figures can be given for the amount handled at the port of New York, and from that estimates can be made with some approximation to the truth for the country generally. The following figures and estimates for the years named are given on the authority of H. R. Chambers, statistician for the New York Mercantile Exchange.

The New York market is figured to have fed during the last five years an average of one million seven hundred and fifty thousand people yearly. The receipts and exports at that port were in packages of fifty pounds each.

| | Receipts. | | Exports. | |
|---|---|---|---|---|
| | Butter. | Cheese. | Butter. | Cheese. |
| 1890 | 1,890,949 | 1,987,217 | 373,982 | 1,496,798 |
| 1889 | 2,044,448 | 1,931,015 | 398,819 | 1,500,930 |
| 1888 | 1,697,909 | 1,993,462 | 140,993 | 1,516,614 |
| 1887 | 1,678,660 | 1,994,857 | 188,541 | 1,450,590 |
| 1886 | 1,648,220 | 1,943,260 | 233,552 | 1,575,268 |

The average receipt yearly, less the average yearly export, will give the average consumption (approximately) of one million seven hundred and

fifty thousand people. 1,785,000 — 266,000 = 1,519,000 packages of fifty pounds each for one million seven hundred and fifty thousand people, or forty-three and one-third pounds for each person, a year as the consumption of butter.

In rural districts the consumption is much greater and the waste is greater, so that an average would bring the personal consumption easily to fifty pounds each, which may be reckoned on the population of the country. Very little under- or over-production seems to exist, if we estimate the great steadiness of price during this period.

The production of butter and cheese of the State of New York for the year 1892 is thus given by the New York State Board of Agriculture in a report published in 1894:

| | | | Pounds. |
|---|---|---|---|
| Number of butter factories | 255, | in which butter was made | 14,024,019 |
| Number of cheese " | 1156, | " cheese " " | 110,605,691 |
| Number of factories making both butter and cheese | 218 | amount of butter in all | 19,497,357 |
| | | " cheese " | 131,148,310 |

The exportation of dairy products from the United States for the last few years has been as follows:

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| Butter (pounds) | 19,373,913 | 31,345,224 | 25,690,025 | 20,247,997 |
| Valued at | $2,937,203 | $4,493,364 | $3,864,765 | $3,263,951 |
| Cheese (pounds) | 36,777,291 | 50,944,617 | 53,167,280 | 38,198,753 |
| Valued at | $3,091,914 | $4,636,063 | $4,509,324 | $3,316,049 |
| Oleomargarine butter (pounds) | 6,063,699 | 4,864,351 | 4,328,536 | 5,549,322 |
| Valued at | $587,269 | $472,856 | $386,297 | $509,703 |
| Oleo oil (pounds) | 103,276,756 | 113,506,152 | 132,579,277 | 142,390,492 |
| Valued at | $8,087,905 | $6,742,061 | $7,904,413 | $9,183,659 |

The production of oleomargarine in the United States for the last few years, according to the returns of the Internal Revenue Department, has been: 1896, 47,023,773 pounds; 1897, 42,534,559 pounds; 1898, 55,388,-727 pounds; 1899, 80,495,628 pounds.

The greater quantity of the "oleo oil" exported from the United States goes to Holland, where it is converted into oleomargarine. The English importation of oleomargarine (or "margarine," as it is officially known there) for the years 1892 and 1893 was as follows:

| | 1892. | 1893 |
|---|---|---|
| Quantity, cwt. | 1,305,350 | 1,299,970 |
| Valued at | £3,712,884 | £3,655,344 |

# CHAPTER VIII.

## VEGETABLE TEXTILE FIBRES.

### General Characters.

ALL the fibres which have been found of technical value for manufacturing purposes may be divided into the two great classes, vegetable fibres and animal fibres, the few found in the mineral kingdom among fibrous minerals being of relatively slight importance in textile manufacturing. Moreover, the distinction is not merely, as the name chosen would indicate, one of origin, but fundamental structural and chemical differences also exist and make themselves evident upon the slightest examination. The vegetable fibres are exclusively cell-growths of relatively simple structure, which during their life form integral parts of the plant organisms, while the animal fibres may be either a hardened secretion like silk or a more complicated cell-growth like wool, distinguished by its scale-like surface.

Thus the vegetable fibres are without exception some form of cellulose $(C_6H_{10}O_5)_n$ in more or less pure condition or an alteration product of the same, while the animal fibres are composed of protein matter, and hence are nitrogenous.

The radical character of their chemical difference just referred to will be more thoroughly appreciated when we note the action of reagents upon the two classes respectively. The vegetable fibres are not dissolved or weakened by alkalies even at a boiling temperature, while the animal fibres are speedily disintegrated, with eventual liberation of ammonia from the nitrogenous material; while, on the other hand, sulphuric or hydrochloric acid rapidly causes a disintegration of the vegetable fibres by their action upon the cellulose, and nitric acid either oxidizes the cellulose or gives rise to nitrated derivatives, while the animal fibres are only slightly affected even when the acids are concentrated. These reactions will be referred to more fully in speaking of the analytical tests used for distinguishing the fibres in mixed goods. (See p. 316.)

The several vegetable fibres may be classified according to botanical or morphological character into three groups: (1) *Seed-hairs* (filaments composed of individual cells); (2) *bast fibres* (filaments or fibre-bundles made up of individual fibre-cells aggregated together); and (3) *fibro-vascular bundles*. Sometimes the term bast fibres is made to include both the second and third classes as just given.

Chemically, all vegetable fibres are composed of cellulose. However, it has long been known that it is frequently more or less contaminated with altered products, which have been known as lignin, ligno-cellulose, adipo-cellulose, etc. The recent researches of Messrs. Cross and Bevan have given us a clear understanding of the nature of the lignin and the alteration products of cellulose. The combination of cellulose and lignin, to which they apply the name of *bastose*, may make up the whole bundle of fibres, as in jute, or may be merely a covering upon the unaltered cellulose.

By distinguishing between the cellulose and the bastose and mixtures of the two we may establish a chemical classification of the vegetable fibres. We are enabled to do this by the aid of the solutions of iodine (potassium iodine solution saturated with free iodine) and sulphuric acid (concentrated glycerine and strong sulphuric acid), which were first proposed by Vétillart.* Pure cellulose when tested with the iodine and sulphuric acid solutions, one after the other, will give a pure blue color, while bastose shows under these conditions a yellow coloration. A complete classification, taking both botanical and chemical characters into account, is the following, which is that of Cross and Bevan's † with some additions:

| | A. Seed-hairs. | B. Dicotyledonous bast fibres. | C. Monocotolydonous fibres corresponding to bast fibres. |
|---|---|---|---|
| Blue reaction with iodine and sulphuric acid. | Cotton. | Linen.<br>Hemp.<br>China-grass.<br>Ramie.<br>Nettle.<br>Sunn fibre. | Straw.<br>Pineapple.<br>Esparto.<br>Alfa. |
| Yellow reaction with iodine and sulphuric acid. | | Hibiscus.<br>Jute. | New Zealand flax.<br>Aloe.<br>Yucca.<br>Manila hemp.<br>Coir. |

1. Cotton Fibre.—The cotton, as already noted, is a seed-hair and envelops the seeds, which are at first enclosed in a capsule. With the ripening of the plant this capsule bursts and the contents spread out widely, constituting the cotton-boll, which is easily picked. The separation of the fibre from the enclosed seed is afterwards accomplished by the mechanical operation called "ginning," in which it is torn from the seed, so that while one end of an individual fibre is always closed the other is irregularly broken.

The genus *Gossypium*, to which all cotton-plants are referred, includes several well-marked varieties, the most important of which are *G. Barbedense*, or "sea-island cotton," grown off the coast of Georgia, South Carolina, and Florida, which yields the longest and strongest fibre or the finest "staple;" the *G. hirsutum*, or upland cotton, grown inland in Georgia, Alabama, Louisiana, and Mississippi, which yields a shorter staple; the *G. herbaceum*, grown in Egypt, Asia Minor, and India; the *G. arboreum*, grown in India and Egypt; the *G. religiosum*, grown in China and India and yielding the so-called "nankin" [illegible] of brown-yellow color; and the *G. Peruvianum*, yielding the [illegible] Brazilian and Peruvian cotton.

The structure of the [illegible] is very characteristic. It presents a flatt[illegible] twisted in spiral form, with compara- [illegible] ning. This structure is illustrated [illegible] the fibre is magnified thirty times [illegible] two hundred times. The first [illegible] fibres distinctly, but the collapsed [illegible] latter feature, however, is shown [illegible]. This flattening is not seen in the [illegible] with liquid protoplasmic matter, but in [illegible] dries up and the walls of the tube

[illegible] sur les Fibres, Paris, 1876.
[illegible] Paper-Making, p. 46.

collapse and flatten out. The adhesion of the fibre to the seed also becomes less, so that the ripe cotton is easily separated in the ginning process. In some species (as in *G. Barbadense*) this separation of hair from the seed is so perfect that the seed shows after the ginning a lustrous black appearance, whence the name locally applied of "black-seed cotton" as distinguished from the upland variety, known as "green-seed cotton."

FIG. 78.

FIG. 79.

The fibre must be picked when mature or it becomes "over-ripe" and deteriorates. The length of the "staple," or fibre, varies considerably with the different varieties of the cotton, the long-stapled sea-island cotton grown on the shores of Georgia and Florida attaining a length of nearly two inches (five centimetres), while the short native cotton of India scarcely exceeds three-quarters of an inch (eighteen millimetres) in length.*

Chemically, the cotton fibre contains about ninety-one per cent. of pure cellulose, seven per cent. of moisture, and small amounts of fat, nitrogenous material, and cuticular substance. An ammoniacal solution of copper oxide causes the cellulose material of the fibre to soften and swell up, whereby the cuticle, which is not softened, takes the appearance of yellowish constricting rings binding the swollen cellulose at regular intervals. Prolonged action of the reagent dissolves the cellulose. When bleached by boiling with sodium carbonate or hydrate, the cuticle is decomposed and the fibre yields easily a very pure form of cellulose.

2. FLAX.—The flax-plant, *Linum usitatissimum*, yields the best known and probably the most valuable of the bast fibres as well as other products, like the linseed oil and linseed cake. (See p. 49.) It is not grown for both fibre and seed together, however, as when the fibre is desired in best [illegible]dition, the plant is gathered before it is fully matured, while if the plant [illegible] ripen fully for production of seed, the fibre obtained is more

[illegible] grown through a wide range of climate, although that [illegible]es, as in India, is chiefly used for seed, the fibre being of [illegible] that grown in colder countries, as in the Russian East [illegible]ds the best fibre. When the plant is cultivated for the [illegible]e, it is either sowed more thickly or, as in Holland and

* Bowman, Structure of the Cotton Fibre, p. 19.

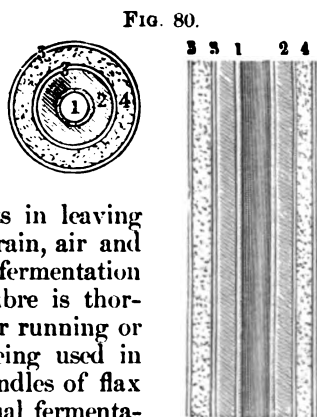
Belgium, forced to grow up through a net-work of brushwood, thus yielding a more slender plant with a longer and finer fibre, known as *lin ramé*. The plant is not cut, but is always carefully pulled up by the roots, and the freshly pulled-up flax is at once submitted to the process of seeding, or "rippling," which is to remove the leaves and seed capsules. This is usually done by hand, drawing the bundles of the flax through upright metallic combs, or "ripples," the prongs of which easily catch the seed capsules, so that three or four drawings suffice to clean the stems or flax straws.

This straw, as it is termed, contains in a dried condition seventy-three or eighty per cent. of its weight of woody matter and encrusting material and twenty to twenty-seven per cent. of bast fibre.

The distinction between the several parts of the stem in the flax and similar plants yielding bast fibres is shown in Fig. 80 by both transverse and longitudinal cross-sections, where 1 represents the pith, 2 the woody tissue, 3 the cambium or partially lignified tissue, 4 the bast fibre, and 5 the crust or rind. To free these several parts of the stem from each other so as to obtain in a clean state the bast fibre is the object of the process of "retting." This is done either by natural means, as in the case of *dew retting* and *cold-water retting*, or by the help of an artificial process, as in *warm-water retting* and *chemical retting*. The dew retting, applied most largely in Russia, consists in leaving the flax thinly spread exposed to dew and rain, air and light, for eight or ten weeks, when, by the fermentation of the pectose matter of the rind, the bast fibre is thoroughly loosened. In cold-water retting either running or stagnant water may be used, the former being used in Belgium and the latter in Ireland. The bundles of flax are placed in crates and submerged, when actual fermentation ensues. The water must be soft water, and care must be taken, especially in the stagnant-water method, to prevent undue heating up during the fermentation. The warm-water retting requires a temperature of 30° to 35° C., and can be carried to completion in fifty to sixty hours, yielding an excellent product. The chemical process consists in the use of dilute sulphuric acid or hydrochloric acid, which allow of the completion of the process in a few days. After the retting process the flax is well washed and dried, and is then submitted to the mechanical processes of "breaking," "scutching," and "hackling" to thoroughly free the fibre from the woody layer and draw out the fibre-bundles into filaments.

FIG. 80.

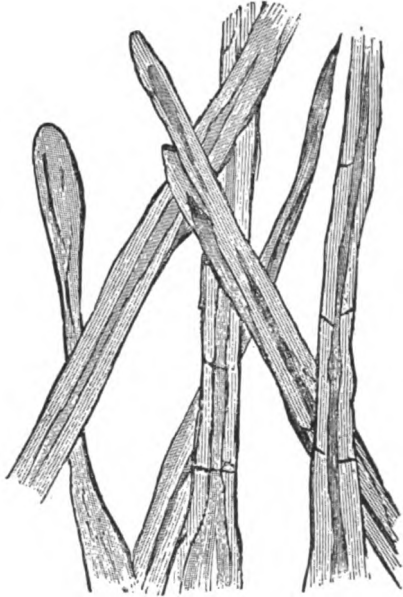


The flax fibre as seen under the microscope seems to be a long straight and transparent tube with thick walls and a minute central canal. Fig. 81 shows these characters of the flax fibre. Characteristic transverse markings also are shown, which may be nodal divisions or slight breaks or wrinkles produced by bending. Longitudinal fissures also show after vigorous rubbing. The linen fibre when cleansed has a blonde or even white color, a fine silky lustre, and great strength. It is less pliant and elastic than cotton but is a better conductor of heat, and hence seems colder than cotton. Chemically it is, like cotton, a pure cellulose, but when swollen by the action of ammoniacal cupric oxide solution does not show the same uniform series of

constricting bands of cuticle. Linen is in many respects more readily disintegrated than cotton, especially under the influence of caustic alkalies, calcium hydrate, and strong oxidizing agents like chlorine and hypochlorites.

3. HEMP.—The fibre known by this name is the product of the *Cannabis sativa*, which is grown for textile purposes chiefly in Russia and Italy, while the seed is grown in India. It is a bast fibre similar to that of the flax-plant, but coarser, stronger, of deeper color and less lustre. Fig. 82 shows the microscopical characters of the hemp fibre. Its cultivation is very

FIG. 81.

Flax ($\frac{350}{1}$).

FIG. 82.

Hemp ($\frac{350}{1}$).

similar to that already described under flax, and differs according as the fibre or the seed are sought. The freshly-plucked hemp loses sixty per cent. of its weight in drying, and from the air-dried hemp straw twenty per cent. of bast fibre is obtained in the case of the male plant and twenty-two per cent. in the case of the female plant. It is used chiefly for ropes and cordage, and the fabric woven from it, known as canvas, is used in sail-making. Much of the finer fibre, however, is combined with linen fibre in weaving other goods. The iodine and sulphuric acid test shows that the hemp fibre is not composed of pure cellulose, but is a mixture of cellulose and bastose.

4. JUTE is the bast fibre of two species of the genus *Corchorus*, and is grown chiefly in India and Ceylon. The fibre is separated from the plant by methods similar to those employed with flax and hemp, the process of cold retting in stagnant water being followed generally. The bast fibres attain a length of 2.5 metres or even more, are of a yellowish-white color, and have a fine lustre. It is seen under the microscope to consist of bundles of stiff lustrous cylinders with walls of very irregular thickness. These characters of the jute are shown in Fig. 83. Chemically, jute differs from the bast fibres

hitherto mentioned in that it contains no free cellulose, but consists of the chemical compound of cellulose with lignin, to which Cross and Bevan, who investigated it, gave the name of *bastose*. It gives, treated with iodine and sulphuric acid, a deep brown color. Moreover, the bastose acts with basic dye colors, like the aniline dyes, as if it had been mordanted with tannin, and can therefore be dyed directly without previous treatment. It is much more easily affected by the action of acids and alkalies than flax or hemp. The influence of air and moisture will also rot the jute fibre. It cannot be bleached safely with chloride of lime because of the readiness with which the fibre is oxidized, but it may be bleached with a weak solution of sodium hypochlorite or by the successive action of potassium permanganate and sulphurous acid. It may be considered as showing more resemblance to the animal fibres in lustre and appearance than any of the other vegetable fibres, and is therefore frequently mixed with wool, mohair, and silk in certain classes of goods.

FIG. 83.

Jute, *Corchorus capsularis* ($\frac{400}{1}$)

Among the fibres of lesser importance which serve as substitutes for hemp and jute are *Manila hemp, Sunn hemp*, and *Sisal hemp*. The first of these is a tropical fibre, obtained on the Philippine Islands from the leaves of the wild plantain. The fibre is obtained by cutting open the leaf-stalks, which are from six to nine feet in length, and then scraping them free from pulpy matter. It furnishes a very superior rope-making fibre because of its combined lightness and strength, and the finer grades are used for woven goods. The color is yellowish or white, and the white variety has a fine silky lustre. It is shown in Fig. 84.

FIG. 84.

Manila hemp ($\frac{250}{1}$).

The Sunn hemp is grown in India, and furnishes a fibre of light-yellowish color and resembles jute, although less lustrous. It is well adapted for cordage and netting.

**Sisal hemp** (or henequen) is derived from the fleshy leaves of a species

of agave grown in Yucatan, British Honduras, and the West Indies and Bahamas. It is used largely in the United States as a substitute for jute in the manufacture of bagging and for cordage, being stronger and lighter than jute.

*Ramie fibre* (*China-grass*).—The bast fibre from two varieties of *Boehmeria nivea*, known in India as Rhea, in the Malay Archipelago as Ramie, and to Europeans as China-grass, has in recent years attracted very favorable attention from all interested in textile industries. It seems to thrive best in the tropics and requires a great deal of moisture. The bast fibre cannot be removed from the woody stems by the retting process used for flax and hemp, as the intercellular substance is so easily decomposed that the water retting rapidly resolves the fibre into a magma of separated cells. The fibre must be removed from the woody stem while the plants are in the green state, as when dried even for several hours' exposure to the sun the fibre becomes difficult to remove from the woody portion. The length of the cells makes it possible to cut the ramie fibre into short lengths and to treat the cleansed fibre like cotton rather than like a long bast fibre. Hence the name "cottonized" ramie which has been applied to that exported from China. With improved methods it is found possible to cleanse it in full lengths, and the fibre is worked like flax rather than with cotton-spinning machinery. The machines for breaking and decorticating the ramie are numerous, but few if any are entirely satisfactory. The properly-prepared fibre is of fine silky lustre, soft, and extraordinarily strong. It is undoubtedly the most perfect of all the vegetable fibres, and will play a great part in the industries of the future, especially as the plant, being a perennial, can be grown continuously for years, spreading of itself very rapidly and yielding several crops yearly. Its cultivation has been begun successfully in Louisiana and Mississippi, and it can probably be extended through the Southern States and Mexico, where it has also been tried. The iodine and sulphuric acid test shows the ramie fibre to be composed of a pure cellulose, which swells easily and voluminously when treated with ammoniacal solution of cupric oxide. The appearance of the China-grass is shown in Fig. 85.

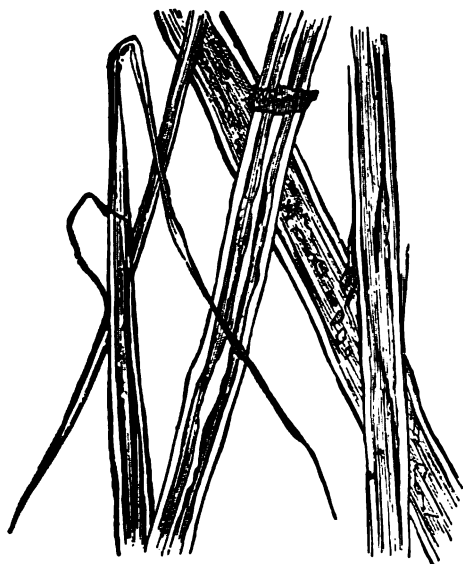



FIG 85.

China-grass ($\frac{140}{1}$).

*Nettle Fibre.*—The bast fibres of the common nettle (*Urtica dioica*) were at one time prior to the development of the cotton industry used extensively in spinning and weaving on the Continent of Europe, the cloth made being known as grass-cloth, the name now given to the product of the China-grass, or ramie. The fibre when cleansed is soft, of good length and strength, and quite lustrous and white. The bast fibres of the linden (*Tilia Europæa*)

and of the paper-mulberry-tree (*Broussonetia papyrifera*) are also used, the former for the manufacture of mats in Russia and the latter by the paper-makers of China and Japan.

*New Zealand Flax* is a fibre obtained from the leaves of *Phormium tenax*, which acquires a length of one to two metres. The fibre as prepared by hand-scraping, the method of the native Maoris, is soft, white, and of silky lustre; as prepared by machinery it is distinctly inferior in character. Its chief value is for rope-making and for coarse textiles. The rope made from this fibre is, however, weakened when wet by sea-water, and therefore must be kept well oiled.

*Pineapple Fibre.*—The leaves of the several varieties of *Bromelia* yield a fine, nearly colorless, fibre, which is worked, especially in Brazil, for the manufacture of the so-called "silk-grass."

*Esparto.*—This is a grass, cultivated especially in North Africa and Spain, where ropes and cordage are made from it. Its chief use, however, is in connection with paper-making. (See p. 282.)

*Cocoa-nut Fibre* (*Coir*).—The coarse fibrous covering of the nut of the coco palm is largely used for brooms, brushes, matting, and coarse carpeting. The fibre is coarse, stiff, very elastic, round, and smooth like hair. It also has great tenacity, and is well adapted for cordage.

The classification of the vegetable fibres just enumerated has already been made upon the basis of the iodine and sulphuric acid reaction according to Vétillart. Two groups were thus established, the one composed essentially of unaltered cellulose and the other of lignified cellulose bastose. Other reactions for these two classes of materials are given in the accompanying table from O. Witt:*

| Reagent. | Cellulose. | Bastose (compound of cellulose with lignin). |
|---|---|---|
| Iodine and sulphuric acid. | Produces blue color. | Produces a yellow or brown color. |
| Sulphate of aniline with free sulphuric acid. | Indifferent. | Colors deep yellow. |
| Basic aniline dyes. | Indifferent. | Produces fast colors. |
| Weak oxidizing agents. | Indifferent. | Rapid disintegration. |
| Ammoniacal cupric oxide. | Immediate solution. | Swelling up, blue color, and slow solution. |

To distinguish the several more important vegetable fibres from each other when admixed, a number of chemical and physical tests have been proposed in addition to the microscopical study of the structural differences already mentioned under the individual fibres.

Thus, according to Kindt's test, the presence of cotton fibre in linen goods can be distinguished, after first removing the size or dressing by thorough boiling with distilled water and drying again, by dipping them from one-half to two minutes, according to the texture of the goods, in concentrated sulphuric acid. They are then well washed with water, rubbed, dipped for a moment in ammonia-water, and dried. The cotton fibre is either dissolved or gelatinized and removed by the rubbing, while the linen fibre remains unchanged or but slightly attacked. By counting the flax fibres remaining for a given superficial area the relative proportion of cotton admixture can be determined.

* Chem. Technologie der Gespinnstfasern, p. 111.

The different effect of strong caustic potash solution upon cotton and linen fibres is also taken as decisive at times, although the difference is not so marked. Both kinds of fibres shrink in size, the cotton fibres remain whitish or grayish yellow, while the linen fibres are colored deep yellow or orange.

A very characteristic test is that given by Boettger. A piece of the mixed goods frayed out in three sides is first dipped in a one per cent. solution of fuchsine, then taken out, washed in running water until this runs off clear, and dipped in ammonia-water for from one to three minutes. The cotton fibre is quickly decolorized, while the linen fibre remains bright rose-red in color. A test easily applied and satisfactory is the oil test, but it is only applicable to white goods which are free from size. The well-dried sample is dipped into olive oil, and then well pressed. The linen fibres become translucent from the capillary action upon the oil, while the cotton fibres remain white and dull in appearance.

An alcoholic cochineal solution (one part of powdered dyestuff digested with twenty parts of alcohol of .847 specific gravity for twenty-four hours) is also recommended by Bolley. Cotton fibres take a clear red color in this solution, while linen fibres are colored violet.

A special test to distinguish the fibre of the *Phormium tenax* (New Zealand flax) from linen or hemp is given by Vincent. It is in the use of concentrated nitric acid, which colors the New Zealand flax distinctly red, but does not change the other fibres mentioned. (For tests to distinguish the vegetable fibres as a class from the animal fibres, see p. 273.)

The use of the microscope, however, is much the most reliable means of distinguishing the several fibres when occurring in admixtures, as the structural character are sufficiently distinct to allow of easy recognition to those possessed of some practice.

## INDUSTRIES BASED UPON THE UTILIZATION OF VEGETABLE FIBRES.

The great utilization of these fibres is of course in the manufacture of textile fabrics of all grades. Having described the fibres which constitute the raw materials of these industries, we shall pass the mechanical side of their treatment and shall note the chemical processes of bleaching, dyeing, and color-printing in a later section of the work (see p. 472), after the preparation of natural and artificial dye-colors has been described. Other industries based upon utilization of some one or more of the vegetable fibres are *Paper-making*, *Pyroxylin and Gun-cotton*, *Collodion*, *Celluloid*, and similar products.

## *A*. PAPER-MAKING.

### I. Raw Materials.

1. RAGS.—The first in order of use for paper-making and still the most important raw materials for the finer grades of paper are linen and cotton rags. As the cellulose of these rags has already undergone a process of purifying from the coloring and incrusting matter with which it was first associated in nature in its preparation for manufacture into textile fabrics, it is well adapted for use in paper-making, the basis of which is also a cellulose fibre. Of course, the rags may be of all grades of cleanliness. They may be cuttings obtained in the course of manufacture of garments,

and being unworn may be relatively clean, or they may be fragments of cast-off wearing apparel gathered from waste-heaps and reeking with filth. Indeed, so great is the demand for paper-making stock that rags are gathered from Japan, Egypt, and all parts of the world, and the bales generally require careful disinfection before they can be used. They may contain sizing and China clay and other loading materials, or they may be colored with various dyes and metallic salts. Rags considered as paper-making stock must therefore be assorted, and for trade purposes they are divided into a large number of grades or classes distinguished by different letters.

Linen rags are distinctly superior for paper-making to cotton rags, as they make a stronger and more durable paper.

2. Esparto.—This grass, mentioned under the vegetable fibres (see p. 280), is of great importance as a paper-making material, particularly in England. The Spanish variety, according to Hugo Müller, contains 48.25 per cent. and the African variety 45.80 per cent. of cellulose, but the yield of bleached fibre obtained in practice probably does not much exceed forty per cent. The fibre is tough and it makes an excellent paper, whether used singly or in admixture with other materials.

3. Straw.—As a material for admixing with other fibres, straw-pulp is largely used. The varieties of straw so utilized are oat, wheat, rye, and barley. Of these, rye is the most suitable on account of its yielding the largest amount of fibre, and next in value is wheat. The amount of cellulose in winter rye is given by Hugo Müller as 47.69 per cent. and in winter wheat as 46.60 per cent., but probably not more than thirty-five per cent. is actually obtained as pulp, much being lost in the treatment on account of the loose aggregation of the cellular tissue. Straw contains more silica than Esparto, and hence requires more soda in the after-treatment to free the cellulose and adapt it for use.

4. Jute.—The "butts" or "cuttings" rejected by the textile manufacturer are largely used in the manufacture of the common grades of paper. It possesses a large percentage of cellulose (63.76 per cent. in the best fibre and 60.89 per cent. in the "butts"), but it cannot be economically bleached to a white color.

5. Manila Hemp.—This is very like jute in its adaptability for cheap and colored papers, and as the fibre is a lignified cellulose it requires considerable boiling with soda to prepare it for use.

6. Wood Fibre.—Two varieties of pulp for paper-making may be obtained from wood,—viz., mechanically and chemically prepared pulp. Of these, the mechanical wood-pulp obtained by shredding the wood serves for the inferior grades of paper only as its fibres are too short and do not "felt" or interlace sufficiently. It can therefore be used only as a filling material. Moreover, the resin present resists strongly the action of bleaching agents, and the paper becomes yellowish after a time. On the other hand, what is termed chemical wood-pulp has met with great favor as a very pure and easily obtainable form of cellulose. Two main processes for its production are now in use, the caustic soda process and the bisulphite process. In the former, the wood chopped up and crushed is boiled under pressure with caustic soda. This is either done in cylindrical boilers at pressures varying from four atmospheres (sixty pounds), as first used by Watt and Burgess, to fourteen atmospheres (two hundred and ten pounds), as used by Sinclair, or by Ungerer's graduated method in a series of nine connected vessels, using low pressures and partly saturated lyes upon the

fresh wood and increasing the pressure and using fresher lyes upon the partly-converted wood. From eighty to ninety per cent. of the soda used is recovered again from the washings. The alkali process is, however, being gradually displaced by the bisulphite process. As first proposed by Mitscherlich, acid calcium sulphite was used. The temperature is brought gradually to 118° C., which is not exceeded, the pressure being from two to three atmospheres. In Ekman's process acid magnesium sulphite is used, and a pressure of from five and a half to six atmospheres is attained. Still another process is that of Franke, which uses bisulphite of lime again. Cross and Bevan explain the efficacy of the bisulphite processes by saying, "The chief agency is the hydrolytic action of sulphurous acid, aided by the conditions of high temperature and pressure; and the subsidiary agencies are, (1) the prevention of oxidation; (2) the removal from the sphere of action of the soluble products of resolution in combination with the sulphite as a double compound, for it is to the class of aldehydes that we have shown that the non-cellulosic constituents of wood belong; and (3) the removal of a portion of the constituents in combination with the base,—*i.e.*, with expulsion of sulphurous acid." The several bisulphite processes, as compared with the ones mentioned previously, yield a larger amount of pure fibre; they preserve its original strength, which is not done when caustic soda acts upon the loosened fibre under pressure, and there is a greater economy of chemicals.

7. PAPER-MULBERRY.—In China and Japan, where the paper-makers excel the best European workmen in the making of some delicate but strong papers, the material chiefly used is the inner bark of the paper-mulberry-tree (*Broussonetia papyrifera*), the leaves of which can be used in feeding silk-worms. The strength of this paper is due to the fact that in making the pulp the long bast-cells are not broken and torn as in European pulping-machines, but merely softened and separated by beating. In taking up the pulp in the mould the cells are made to lie in one direction, and the paper may be strengthened by taking one or more dips in which the cells are made to lie in other directions. Some gum is added to make the cells of the pulp adhere.

## II. Processes of Treatment.

1. MECHANICAL PREPARATION OF THE PAPER-MAKING MATERIAL.—This differs, of course, according as the raw material is composed of rags, Esparto, straw, or other cellulose-containing substance. With rags, a preliminary sorting always takes place, more or less complete according to the make-up of the bales. Numerous commercial designations are in use for these different grades so obtained. We need only speak of white linen, blue or gray linen, white cotton, colored linen or cotton, sacking, half wool, etc. They are then cut into coarse fragments by hand, being passed rapidly over broad knives fixed at a set angle in tables, and all buttons and hard substances removed. A thorough dusting or "thrashing" is now necessary to remove the dust and detachable dirt. This is effected in large wooden boxes with revolving arms. A more thorough cutting now ensues with the aid of revolving knives, followed in most cases by a final and thorough dusting, so as to eliminate as much dirt as possible and save in the amount of boiling necessary as the next operation.

With Esparto a mechanical sorting or "picking" is also the first operation. The grass is spread out on tables and the weeds, root-ends, etc., carefully removed, as these would be difficult to boil and bleach and would give

rise to dark-colored specks in the finished paper known as "sheave." Machines for this cleansing of the Esparto are also used quite largely.

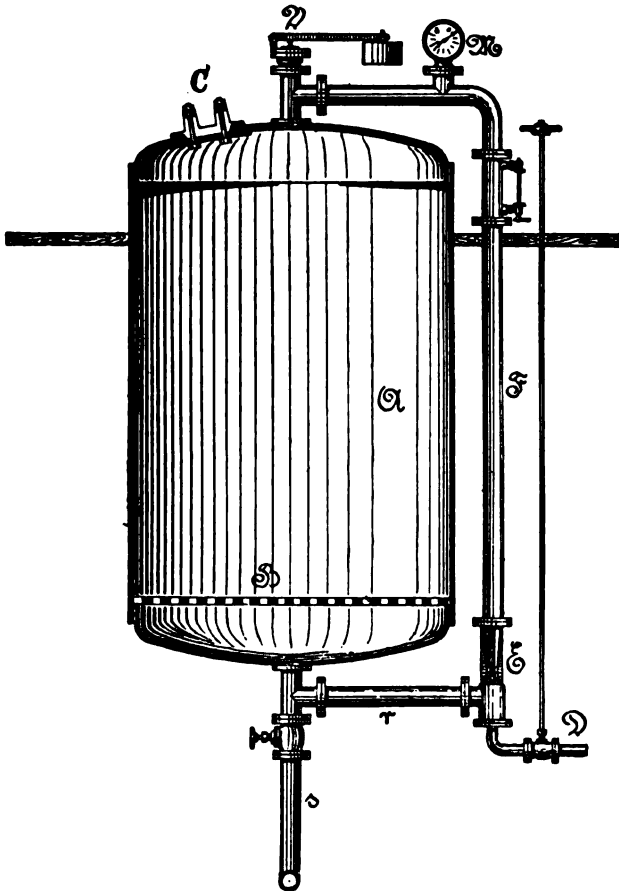
The preparation of mechanical and chemical wood-pulp has already been referred to.

2. Boiling.—The boiling of the rags with caustic soda, caustic lime, or a mixture of soda ash and lime, which is the next operation, is designed to free them from grease, dirt, and coloring matter. This may be done either in rotating spherical or cylindrical boilers or in the so-called "vomiting" boilers described later. The boilers are often large enough to take two tons of rags at a charge. The amount of alkali usually ranges from five to ten per cent. on the weight of the rags. Soda is preferred by many paper-makers to lime on account of the greater solubility of the compounds it forms, although both are in general use. The time of boiling varies from two to six hours, according to the quality of the rags, the alkali employed, and the pressure. The use of high pressures is to be avoided as far as possible, as it may result in fixing the dirt and coloring matter instead of dissolving them. A pressure of from three to four atmospheres is commonly employed. After the pressure has been allowed to fall, the liquor collected at the bottom of the boiler is drawn off and water run in to give the rags a slight preliminary washing. The charge is then drawn off.

In the case of Esparto, the "vomiting" boiler or other form of apparatus for keeping up a continuous circulation of the liquor is used. A form of boiler in which this circulation is kept up by the use of a steam injector is shown in Fig. 86. The grass is put in through the man-hole *C* and rests upon the false bottom *B*. Circulation is set up by the steam from the pipe *D* passing through the injector *E* and drawing the liquor through the small pipe *r*. In order that this circulation may proceed uniformly, it is necessary that the steam shall enter at a pressure one atmosphere higher than the pressure existing in the boiler. A manometer, *M*, shows the pressure, and a safety-valve, *V*, allows of the adjustment of the necessary conditions. The contents of the boiler are discharged through *s* at the end of the operation. The boiling takes from four to six hours. The quantity of soda necessary depends upon the nature of the grass, Spanish requiring less than African, and the pressure employed varies from five to forty-five pounds per square inch.

3. Washing.—This operation, which must be a thorough one, takes place in a washer or "breaker." The name "hollander" is very generally given to this machine as well as to the similar one in which the beating or mixing is done. The hollander is an oval iron tub, from ten to twenty feet long, four to six broad, and about three feet high, divided for two-thirds or more of its length by an upright partition known as the "mid-feather." The details of its construction may be seen from Figs. 87 and 88. The roll *A* carries upon its circumference a number of steel knives and revolves on one side of the "mid-feather," or longitudinal division *Q Q* (Fig. 88). The floor on this side is raised in a way as to bring the pulp well under the roll, as shown by the line *J O K* (Fig. 87). Immediately under the roll is the "bed-plate," shown at *O*, and provided with knives similar to those in the roll *A*, but set with their edges in the opposite direction. The distance between the roll and the bed-plate can be [illegible]ried at will by means of the hand-wheel *h* and the mechanism shown [illegible] and *i* (Fig. 88). After passing between the roll and the bed-plate, [illegible]lp flows down the "back-fall" *K K*, and finds its way around to the

other side of the mid-feather. On the inclined part of the floor and immediately in front of the bed-plate a small depression is made at *E*, covered with an iron grating, for the purpose of catching buttons, small pieces of stone, and other foreign substances that may have found their way into the rags or other paper stock. The dirty water from the rags is removed by the "drum-washers" *R R*. The ends of the drums are of wood, and the circumference is covered with fine copper or brass wire-cloth. The wash-water

Fig. 86.

passes through the wire-cloth into the compartment shown in *R*, and passing towards the narrower end of the inner conical tub, flows out through the side of the drum into a trough placed to receive it.

In washing the rags in this machine, the tub is partly filled with water, the rags from the boiler dumped in, and the operation begun. The action of the roll thoroughly mixes pulp and water and sweeps the rags up the incline and over the back-fall *K*. The dirty water then passes away through the drum-washer, the supply of pure water being so regulated as to keep the level constant. When the water begins to run off clear the

supply is stopped, the washer still being kept in action. As the level falls, the drum is lowered by means of the handle *h*. When sufficiently drained, the pulp is discharged through the valves *C C* in the bottom of the washer. It is now ready to be bleached. This may be done in the washer itself or in separate engines called "potchers." If done in the washer, a solution of bleaching-powder is run in after the withdrawal of the wash-water and the action of the roll continued.

FIG. 87.

Esparto is generally washed in exactly the same way as that just described for rags, but in some mills the grass is washed in a series of connected lixiviating tanks like those used in alkali-works. Pure water flows in at one end, passes through fresh lots of grass in succession, and issues at the farther end highly charged with the soluble products of the grass. The washed and broken pulp now goes by the name of "half-stuff."

4. BLEACHING. — This is done with the aid of chlorine or a solution of calcium or sodium hypochlorite. The use of chlorine gas, once largely practised, has been almost entirely superseded by the hypochlorite solutions, as chlorine is liable to form difficultly removable compounds, and it also tends to attack and weaken the fibre of the pulp. When chlorine is used, 2.5 to 5 kilos. of salt are taken as needed for 100 kilos. of "half-stuff."

The solution of calcium hypochlorite must be used perfectly clear and free from undissolved hydrate or carbonate. A solution of 6° Twaddle, which contains about half a pound of bleaching-powder to the gallon, is commonly used. An addition of hydrochloric or sulphuric acid to the bleaching-liquor is sometimes made, but this must be done with care so as not to liberate chlorine instead of hypochlorous acid. This danger from

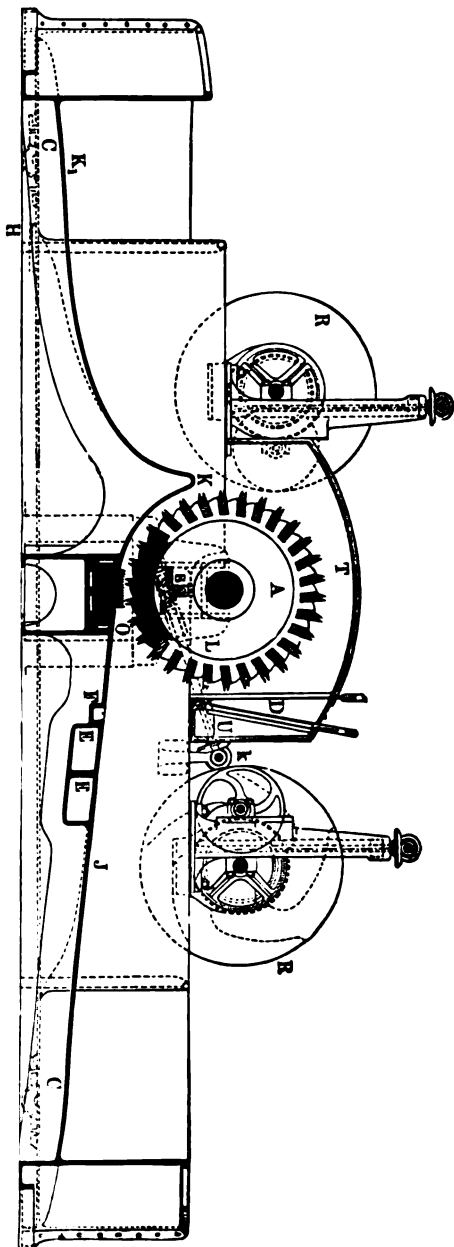
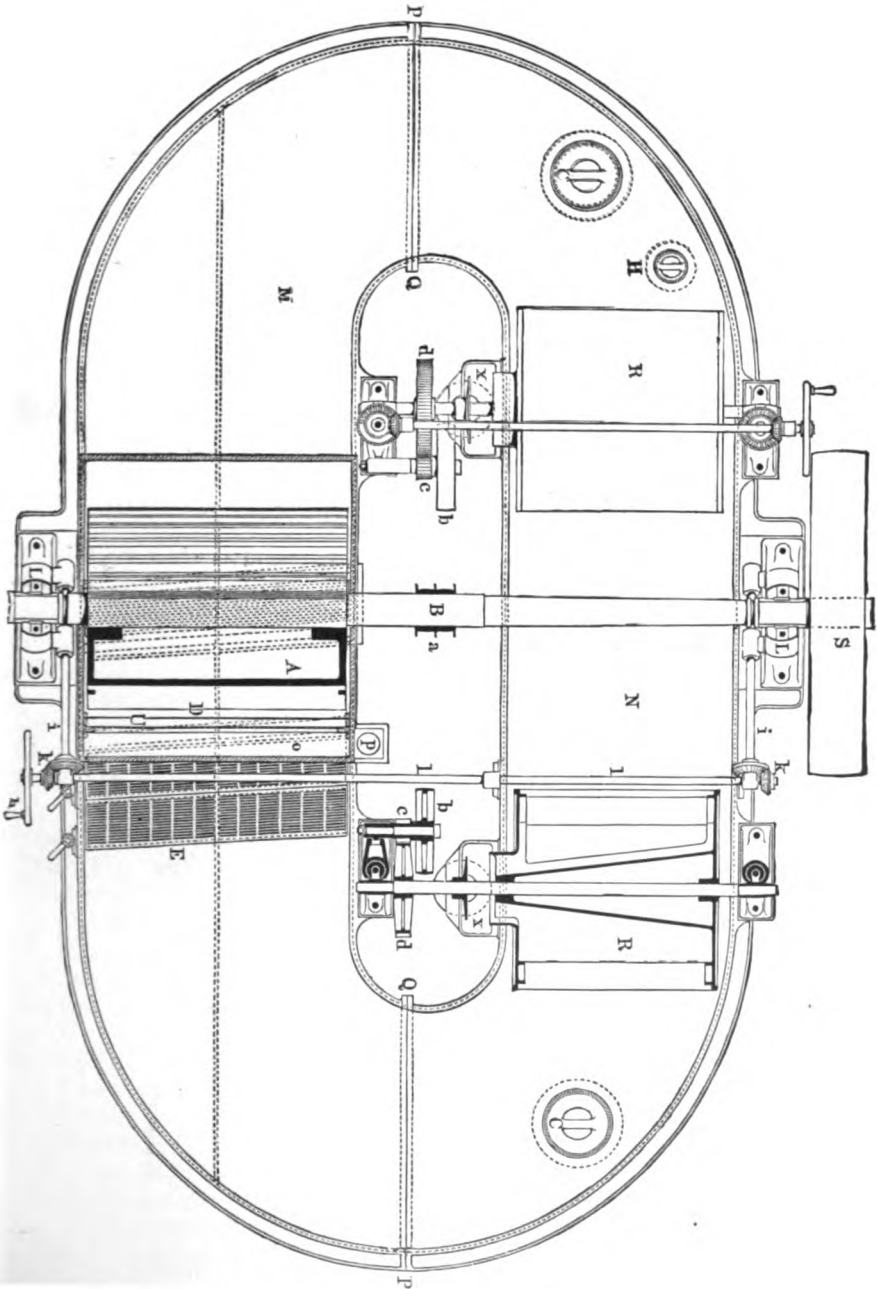



**Fig. 88.**

free chlorine is greater when highly lignified fibres, such as wood or jute, are used. The bleaching is often effected by combining a preliminary treatment in the "potcher" or washer with a subsequent prolonged steeping in tanks. A process has been recently proposed by Professor Lunge involving the use of acetic acid. The quantity required is very small, as during the process of bleaching it becomes regenerated. Any free lime in the solution is first nearly neutralized with a cheaper acid, such as hydrochloric or sulphuric acid, followed by the addition of the acetic acid. The process is said by Cross and Bevan to give excellent results with high-class material, such as the best cotton and linen rags, but is not to be recommended for materials like straw or Esparto.

A process invented by Thompson is also said to be very effective for the bleaching of rags. It consists in saturating the material with a weak solution of bleaching-powder and then exposing them to the action of carbonic acid gas. The bleaching action is thus made very rapid and effective.

One of the most recent innovations in bleaching is the application of electricity in this connection. The only process that has yet attracted much attention is that of M. Hermite. It is thus described by Cross and Bevan:* "This process is based upon the electrolysis of a solution of magnesium chloride, this salt having been found to give the most economical results. The solution, at a strength of about 2.5 per cent. of the anhydrous salt ($MgCl_2$), is electrolyzed until it contains the equivalent of about three grammes of chlorine per litre. This solution is then run into the 'potcher' containing the pulp to be bleached; a continuous stream is then kept up, the excess being removed by means of a drum-washer. This excess, which, after being in contact with the pulp in the engine, is more or less deprived of its bleaching properties, is then returned to the electrolyzing-vat, where it is again brought up to normal strength. The electrolyzed solution has been found to possess very remarkable properties which have considerable bearing upon the economy of the process. If a solution be taken of equal oxidizing efficiency with one of calcium hypochlorite, as indicated by the arsenious acid test, it is found that the former possesses greater *bleaching* efficiency than the latter in the proportion of five to three. Moreover, the bleaching is much more rapid and the loss of weight which the substances undergo is less for equal degrees of whiteness obtained." Further details of this process will be found in the article by Cross and Bevan in the "Journal of the Society of Chemical Industry," for April, 1887.

The removal of any excess of chlorine or bleaching-liquor must now be looked to. This is done either by careful washing or by the use of an "antichlor." The first method has the advantage of not only removing the bleach but also of the chloride of calcium which has been formed from it. It, however, takes some time and consumes a large amount of water. Much more general is the use of an "antichlor." The commonest of these is sodium thiosulphate (or hyposulphite, as it is commonly called). This is ordinarily decomposed according to the reaction $2(Ca(ClO)_2) + Na_2S_2O_3 + H_2O = 2CaSO_4 + 2HCl + 2NaCl$, but when the solutions are very dilute, sodium tetrathionate, $Na_2S_4O_6$, and caustic soda and lime are formed. For the first equation two hundred and forty-eight parts of commercial thiosulphate are required to neutralize four hundred and nine parts of bleaching-powder of thirty-five per cent. available chlorine strength. The various

* Text-book of Paper-Making, p. 115.

sulphites are also in use as antichlors, sodium sulphite being the most important. A cheap antichlor is also made by boiling together lime and sulphur, the resultant calcium sulphide solution containing a mixture of calcium thiosulphate and calcium pentasulphide. This last-mentioned preparation is, however, objectionable on account of the free sulphur formed, as this affects the pulp injuriously. Whatever antichlor is used, an excess should be avoided, as it may act upon the color or size added subsequently. . The antichlor should therefore be added in successive small portions, and any hypochlorite solution still remaining be tested for from time to time with iodide of starch paper, which will be turned blue as long as hypochlorite remains.

5. BEATING.—The bleached pulp, or "half-stuff," is not yet in condition for making an even paper, as the fibre has not been sufficiently disintegrated. This is now effected in the beating-engine, which is a hollander very similar to the breaker already illustrated, except that the roll carries more knives and it is usually let down much nearer the bed-plate. The half-stuff is furnished in successive portions to the beater previously partially filled with water, each successive portion being allowed to mix thoroughly with the water before another lot is added. This is continued until the mass is so thick that it will only just turn round under the action of the roll. The operation of beating is designed to be a more complete breaking or tearing apart of the fibres rather than a cutting, as this latter result would interfere with the felting of the fibres so necessary in paper-making. Cotton and linen rags naturally take longer than most other paper-making material, taking often as much as ten hours; wood-pulp requires to be very gently and slowly beaten, so that it requires some six hours; while Esparto is sufficiently disintegrated in from two to four hours. In making the finer grades of paper, the roller bars or knives instead of being made of steel are made of bronze, so that contamination with oxide of iron is avoided.

Beaters of a totally different form of construction are also largely in use. Thus, in the Jordan beater the roll is in the shape of a truncated cone, fitted with knives and revolving in an iron box of corresponding shape, and also fitted with knives set at an angle. In the Kingsland engine and the Gould engine a circular plate furnished with knives revolves against one or more stationary plates similarly fitted, somewhat after the manner of millstones. The half-stuff is even more thoroughly disintegrated in these beaters than in the ordinary forms.

6. LOADING, SIZING, COLORING, ETC.—Except in the very finest papers, some mineral-loading material is incorporated with pulp when in the beater. This is, of course, in the main for cheapening purposes, but also serves the useful purpose of filling the pores of the paper and enabling it to take a better surface in the subsequent operations of calendering. Such loading materials are China clay, or kaolin, sulphate of lime, or "pearl hardening," barium sulphate, precipitated chalk, bauxite, precipitated magnesia, and magnesium silicate, or "agalite." The amount added varies from two to three per cent. to twenty per cent., or in rare cases even more.

All papers except blotting-papers have also to be sized. This is for the purpose of filling the pores with some material that will, to some degree at least, resist the action of water. Thus, all writing-papers, and in general printing-papers also, are sized to prevent the ink applied to them from running. This is done either by what is termed "engine-sizing"—that is, in the beating-engine itself—or by "tub-sizing," when the paper as it goes

through the Fourdrinier machine (see below) passes through a tub of gelatine size and takes a layer of the same on either surface.

In "engine-sizing" a rosin soap is first added to the pulp in the beater, and when this is thoroughly incorporated a solution of alum is run in, forming, as it has been generally supposed, a resinate of alumina, which is water resistant when dried. Wurster * claims to have shown, however, that the sizing in this case is not due to the formation of a resinate of alumina but to a separation of free resin, and in this result he has been supported by Conradin.†

With the resin soap is also added some starch, and the quantity of mixed rosin and starch is usually from three to four pounds to the one hundred pounds of pulp.

The pulp although bleached is rarely white enough to produce a clear white paper, and the yellowish tint requires to be neutralized by the addition of small quantities of blue and pink coloring material. Ultramarine, smalt, and aniline-blue are used for the first color, and either cochineal, Brazil-wood, or aniline-red for the second. The paper may be colored throughout any desired color by using rags previously dyed, or by adding to the bleached pulp in the beater the necessary dyes or pigments.

7. Manufacture of Paper from the Pulp.—We have to consider here two different products,—viz., hand-made paper and machine-made paper. The former is made by taking in the mould upon the "deckel," or wire-cloth frame, just sufficient of the prepared pulp diluted with water to make a sheet of paper. As the water drains through the wire-cloth and leaves the fibres spread out upon the surface, the felting operation is assisted by shaking the frame gently from side to side. The mould with the sheet of paper is then turned over, and the sheet thus transferred from the wire to a piece of felt. When a number of sheets have been thus prepared, they are piled up with alternate sheets of felt and the whole subjected to strong pressure to expel water. They are then sized if required by dipping them into a solution of gelatine, again pressed, and hung up to dry. When dry they are calendered or pressed between hot metal rolls.

Machine-made paper is made on what is universally known as the Fourdrinier machine, of which an improved form, as manufactured by the Pusey and Jones Company, of Wilmington, Delaware, is shown in Fig. 89. We cannot here describe the various mechanical details of this machine, but may summarize by saying that it consists of an endless mould of wire-cloth on to which the prepared pulp flows from the "stuff-chest" through a "regulating-box" and over the "sand-table" and the "screen." From the deckel wire it now passes through a series of rolls, at first covered with felt and later of smooth heated metal known as the "dandy-roll," the "couch-rolls," the "press-rolls," the "drying cylinders," and, finally, the "calenders." The action of the machine is a continuous one, and the speed of the Fourdrinier is from sixty to two hundred and forty feet per minute,—the latter for cheap newspaper, the former for the best paper requiring the most care.

What is known as "tub-sizing" is applied to many machine-made papers in the course of their passage through the Fourdrinier. A filtered solution of gelatine is used to which about twenty per cent. of its weight of alum has been added. A certain quantity of soap is also often added, a white soap free from resin being used.

Instead of the Fourdrinier, what are termed cylinder-machines are also

* Wagner's Jahresbericht, 1878, p. 1155. † Ibid., 1879, p. 1106.

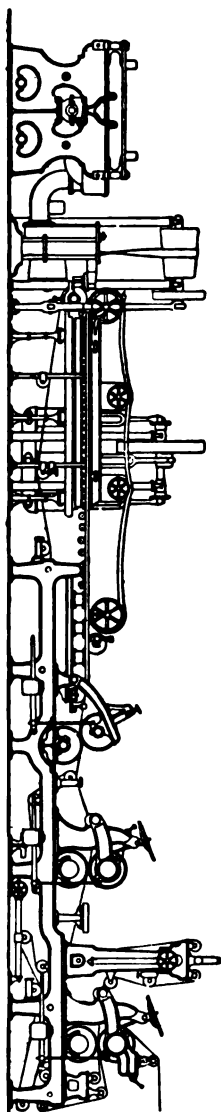
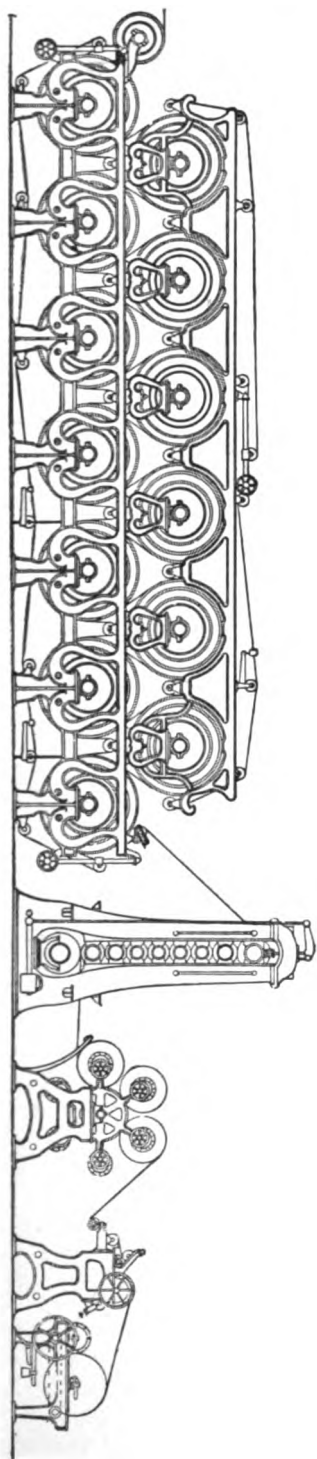



FIG. 91.

in use, in which a large drum or cylinder covered with wire-cloth revolves in the vat containing the pulp. As it revolves the fibres attach themselves to the wire and the water is sucked through the meshes by a partial vacuum within. The sheet of paper thus formed is taken on to an endless felt passing over a couch-roll, which revolves in contact with the hollow drum, and thence passes to a large drying cylinder heated by steam. Paper made on such a machine is weaker, however, than that made on the Fourdrinier, because it has not been found possible to give the shaking motion to the cylinder necessary to produce the felting of the fibres.

## III. Products.

The products are almost without number, and vary not only in different countries, but even locally from time to time as different mills change their production. We will therefore attempt only a general classification of the main varieties.

1. Blotting- and Tissue-paper.—These are unsized papers. Blotting-paper is a mass of loosely-felted fibres, which, however, is free from any loading or filling material, and therefore is capable of easily and quickly taking up water or other liquids. It may be white, gray, or colored to any shade by the addition of the proper dyes. Tissue-papers, which as the name indicates are the thinnest of all papers, are made from very strong fibres, such as that of hemp-bagging and cotton canvas, and on machines somewhat different from the ordinary Fourdrinier.

2. Wrapping-papers.—These are partially-sized papers of coarse materials, such as straw, jute, Manila hemp, common rags, etc. They may show the natural color of the materials or may be colored, as in the case of the blue wrapping-paper commonly used for packing sugar. A more strongly sized and calendered wrapping-paper is made for use with linens and other textile goods.

3. Printing-papers.—These are white papers, generally with filling and sizing material, although some special grades are given a smooth surface by calendering instead of sizing. The cheaper grades for newspaper use are frequently largely adulterated with filling material, and mechanical wood-pulp is also largely used in their manufacture.

4. Writing-papers.—These are thoroughly-sized papers, for which the best materials are generally used, linen rags alone being taken for the finer grades.

5. Cardboard, Pasteboard, and Papier-maché.—Pasteboard may be made by pressing a number of sheets of freshly-formed unsized paper in powerful presses, or cementing them together by the use of glue or other cementing material, and then pressing the mass so formed. Cardboard is made direct upon machines adapted for heavy layers of pulp and pressed and calendered like similar grades of ordinary paper. Papier-maché is made chiefly from old paper by boiling to a pulp with water, pressing, mixing with glue or starch paste, and then pressing in moulds previously oiled. After drying, the articles are soaked with linseed oil and then dried at higher temperature.

Parchment-paper.—If a pure unsized paper be dipped in sulphuric acid of 60° B. a portion of the cellulose is changed into *amyloid* (hydrocellulose, according to Girard), which forms a gelatinous coating over the swollen fibres and effects in some degree a sizing of them. The paper is

made hereby translucent and parchment-like, the strength is increased from three to fourfold, and the specific gravity by perhaps forty per cent. For the manufacture of this parchment-paper the long-fibred, unfilled paper is to be chosen. After treatment the paper is quickly washed, first with water, then with weak ammonia, and again with water.

In place of sulphuric acid we have the treatment with ammoniacal cuprous oxide solution or zinc chloride. The former reagent furnishes the *Willesden ware*, which always retains the light blue-green color; the latter yields the valuable product known as *indurated* or *hard fibre*. In preparing this latter material the paper, which is either unsized or prepared with a rosin size and then nearly dried, is dipped or run while in the roll through a bath of zinc chloride of about 65° to 70° B. kept at a temperature of about 38° C. After passing through the zinc chloride bath, the paper is passed over hot rolls and then cooled and washed in pure water to remove all excess of zinc chloride or rosin size. It is then dried in a heated room, given a coating of paraffine oil, and calendered. The material so obtained is very strong, tough, and can be washed.

6. SIDE-PRODUCTS.—*Recovered Soda.*—The alkaline liquors in which rags, esparto, and other paper-making material have been boiled were at one time run off as waste products. This is no longer done in properly conducted mills, as the alkali used can be recovered in the form of carbonate by evaporation of the waste-liquor and ignition of the residues, and this carbonate can then be causticized and fitted for renewed use. The soda during the process of boiling with the paper-making materials takes up a large amount of non-cellulose fibre constituents, such as resin, coloring matter, and silica. These on evaporation and ignition become either carbonate or silicate. It will not be possible for us here to describe the forms of evaporators in use for this soda recovery. One of the best-known evaporators is that of Porion, used largely in England and on the Continent. For a description of this and other forms, see Cross and Bevan's "Text-book of Paper-Making," p. 182. The Yaryan multiple-effect evaporator (see p. 131) is also being introduced for concentration of the spent liquors.

The recovered soda consists essentially of carbonate of soda, together with a certain amount of silicate of soda if the liquor had been obtained by boiling straw or Esparto. The causticizing is done in the usual way with caustic lime and the clear alkali decanted from the separated calcium carbonate, which is then thoroughly washed.

## IV. Analytical Tests and Methods.

1. DETERMINATION OF THE NATURE OF THE FIBRE.—This may be done in part, if not wholly, by either of two methods,—viz., by the aid of the microscope or by the use of chemical tests for individual fibres. The fibre is always torn or cut and often somewhat attacked. By some practice, however, it is possible to distinguish between cotton and linen or to identify both in admixture. Wood and straw can also be identified. In making these tests, it is best to take strips of the paper in question and boil them in succession with alcoholic potash solution, with water, with two per cent. hydrochloric acid, and then again with water. If they are now shaken up with a little warm water, we obtain a fine magma of fibres, which when mixed with an equal volume of glycerine is well adapted for examination under the microscope. The distinctive characters of some of the chief

paper-making materials as seen under the microscope may be thus summarized, according to Cross and Bevan:* *Cotton*,—flat, ribbon-like fibres, frequently twisted upon themselves. The ends generally appear laminated. *Linen*,—cylindrical fibres, similar to the typical bast fibre. The ends are frequently drawn out into numerous fibrillæ. *Esparto*,—the pulp consists of a complex of bast fibres and epidermal cells. The most characteristic feature of Esparto pulp is the presence of a number of fine hairs which line the inner surface of the leaf, some of which still remain after the boiling and washing processes. The presence of these hairs may be taken as conclusive evidence of the presence of Esparto. *Straw*,—this closely resembles Esparto-pulp in microscopical features, except that the hairs are absent. On the other hand, a number of flat oval cells are always present in paper made from straw. *Chemical wood-pulp*,—flat ribbon-like fibres, showing unbroken ends. The presence of pitted vessels is eminently characteristic of pulp prepared from pine-wood. *Mechanical wood-pulp* may be recognized by the peculiar configuration of the torn ends of the fibres and from the fact that the fibres are rarely separated, but generally more or less agglomerated. The pitted vessels of pine-wood also show, and usually more distinctly than in chemical wood-pulp.

The chemical reagent most useful in testing paper-pulp is aniline sulphate. With most of the fibres which consist of cellulose simply it gives no reaction. Straw, Esparto, and mechanical wood-pulp can, however, be identified by its means. Thus, where paper containing straw or Esparto is treated for some time with a boiling one per cent. solution of aniline sulphate, a pink color is produced. Esparto gives the reaction with greater intensity than straw. Mechanical wood-pulp treated with this solution develops even in the cold a deep-yellow color. According to Bolley,† the moistening of paper containing mechanical wood-pulp with nitric acid will give the same result, and a naphthylamine salt produces a deeper orange color. According to Wiesner, phloroglucin is also a delicate reagent for wood fibre in paper. A drop of dilute solution of phloroglucin put upon the paper and this followed by moistening with hydrochloric acid develops an intensely red color. Fuchsine also colors wood fibre red, but has no effect upon paper from linen fibre alone.

M. Wurster in "Journ. de Pharm. et Chemie" has extended Wiesner's observation on phloroglucin to a number of the phenols, finding them as a class to serve as reagents for distinguishing between wood-pulp and other cellulose. The results are:

| Reagent. | Wood-pulp. | Cellulose paper. |
|---|---|---|
| Orcin | Dark red. | No color. |
| Resorcin | Deep green. | Violet. |
| Pyrogallol | Blue-green. | Violet. |
| Phenol | Yellow-green. | Violet. |
| Phloroglucin | Blue-violet. | No color. |

According to Godeffroy and Coulon, mechanical wood-pulp from pine-wood possesses the property, after it has been extracted with water, alcohol, and ether, of reducing gold solutions on boiling. This property is not possessed by wood-pulp prepared by the caustic soda or sulphite processes, after similar extraction with solvents, nor by the pulp prepared from linen or

* Text-book of Paper-Making, p. 199.

† Handbuch der Technisch-Chem. Untersuchungen, 6te Auf., p. 1006.

cotton fibres. This property depends upon the fact that in mechanical wood-pulp ligno-cellulose remains, and to this composition is due the reducing power upon gold solutions. This ligno-cellulose is destroyed in the preparation of chemical wood-pulp, and does not exist at all in the linen or cotton fibre. It has been found that on the average one hundred parts of mechanical wood-pulp, extracted with solvents and dried at 100° C., will reduce fourteen thousand two hundred and eighty-five grammes of gold. It is thus made possible by weighing the reduced gold to estimate the amount of mechanical wood entering into the composition of the paper. For details of the analytical method based upon this gold reaction, see Bolley's "Handbuch der Technisch-Chem. Untersuchungen," 6te Auf., p. 1007.

2. Determination of the Nature of Loading Materials.—The total amount of the mineral-loading material is determined by igniting a weighed quantity of the paper until the ash is white or grayish and then accurately weighing this. The ash from a paper containing the China clay is insoluble in boiling dilute hydrochloric acid; that from paper containing calcium sulphate is soluble, and deposits on standing needle-shaped crystals of gypsum easily recognizable by chemical tests.

3. Determination as to Nature of the Sizing Materials.—The iodine test serves to indicate the use of starch in the size, as it produces the well-known blue color. Extraction of the paper with alcohol containing a few drops of acetic acid serves to show the resin used in the size. The alcohol, after cooling, is poured into four or five times its bulk of water, when the resin separates, producing cloudiness or turbidity. Or, after extraction, the alcohol is evaporated, leaving the resin capable of being identified by its properties. Notable quantities of alumina in the ash also point to the use of resinate of alumina as sizing material. According to Wurster, if between two sheets of paper which have been sized with resin is pressed paper moistened with tetramethylparaphenylen-diamine solution, a bluish-violet color is produced, while paper free from resin is not affected. Boiling of the paper sample with distilled water, filtering, and adding a few drops of tannic acid solution will serve to show the presence of gelatine sizing. If present, a white curdy precipitate is formed on the addition of the tannic acid.

4. Determination of the Nature of the Coloring Material.—In deciding as to the presence of coloring matter, we must bear in mind the reactions of the commoner pigments used. Ultramarine is destroyed and decolorized on addition of acids; Prussian blue is decolorized by heating with alkalies; indigo is decomposed by heating with chlorine or nitric acid; smalt withstands the action of both acids and alkalies and remains in the ash as a blue glass; the aniline colors are capable of extraction with alcohol as solvent.

## *B*. GUN-COTTON, PYROXYLINE, COLLODION, AND CELLULOID.

### I. Raw Materials.

The basis of these preparations is the class of nitrates formed from cellulose by the action of nitric acid, either taken singly or admixed with strong sulphuric acid, or as developed by the action of sulphuric acid upon a nitrate. Using the doubled formula $C_{12}H_{20}O_{10}$, we may note the following five stages of nitration:

*Hexanitrate*, $C_{12}H_{14}O_4(NO_3)_6$ (trinitro-cellulose, $C_6H_7(NO_2)_3O_5$, of other

writers), is the true gun-cotton. It is formed by the action of a mixture of the strongest nitric acid (specific gravity 1.52) with two or three parts of concentrated sulphuric acid, in which the cotton is immersed for twenty-four hours at a temperature not exceeding 10° C. (56° F.). The hexanitrate so prepared is insoluble in alcohol, ether, or a mixture of both, in glacial acetic acid or in methyl alcohol. Acetone dissolves it very slowly. According to Eder, the mixtures of nitre and sulphuric acid do not give this nitrate.

*Pentanitrate*, $C_{12}H_{15}O_5(NO_3)_5$. It is difficult, if not impossible, to prepare this nitrate in a state of purity by the direct action of the acid upon cellulose. The best method (that of Eder) is to dissolve gun-cotton (hexanitrate) in nitric acid at about 80° to 90° C. (176° to 194° F.) and then precipitate as pentanitrate by concentrated sulphuric acid after cooling to 0° C.; after mixing with a larger volume of water and washing the precipitate with water and then with alcohol, it is dissolved in ether-alcohol and again precipitated with water, when it is obtained pure. This nitrate is insoluble in alcohol, but dissolves readily in ether-alcohol and slightly in acetic acid. Strong potash solution converts this nitrate into the dinitrate, $C_{12}H_{18}O_8(NO_3)_2$.

The *tetranitrate* and *trinitrate* (collodion pyroxyline) are generally formed together when cellulose is treated with a more dilute nitric acid and at a higher temperature and for a much shorter time (thirteen to twenty minutes) than in the formation of the hexanitrate. It is not possible to separate them, as they are soluble to the same extent in ether-alcohol, acetic ether, acetic acid, or wood-spirit. On treatment with concentrated nitric and sulphuric acids, both the tri- and tetranitrates are converted into pentanitrate and hexanitrate. Potash and ammonia convert them into dinitrate.

The *dinitrate*, $C_{12}H_{18}O_8(NO_3)_2$, always results as the final product of the action of alkalies on the other nitrates, and also from the action of hot, somewhat dilute nitric acid upon cellulose. The dinitrate is very soluble in ether-alcohol, acetic ether, and in absolute alcohol.

The chief raw material for the manufacture of these nitrates at present is the waste from cotton-spinning, which has already been freed from the impurities of the raw cotton. It is first picked clean by hand from admixture with foreign matter and then torn and opened up by machinery so as to fit it for easy action of the nitrating acids. It is then treated for a few minutes with boiling potash solution, thoroughly washed, and dried by steam. For the manufacture of celluloid a specially prepared and perfectly pure tissue-paper is now used, which is torn into shreds by machinery preparatory to the nitrating.

## II. Processes of Manufacture.

1. Gun-cotton.—The following is the procedure at Waltham Abbey, where gun-cotton is made for the English government under Sir F. Abel's improved method. A mixture of fifty-five parts of nitric acid (1.516 specific gravity) and one hundred and sixty-five parts of sulphuric acid (1.842 specific gravity) is taken for one part of cotton. The nitrating mixture is placed in cast-iron vessels, cooled from without by flowing water, and the cotton immersed. It may either remain in these until ready for washing, or may after a brief immersion be transferred to smaller stone-ware vessels, similarly cooled, in which it then remains for twenty-four hours, for the double purpose of completing the nitration, so that the product shall con-

tain a maximum of the highest, or hexanitrate, and of allowing the contents of the jar to cool down perfectly. The nitrated cotton is then centrifugated, stirred up thoroughly with cold water, again centrifugated, and then washed systematically with warm water to which some soda has been added. The gun-cotton so obtained may either be used in the loose form or, when designed for manufacture into cartridges, is beaten in a hollander after the manner of paper-pulp, and then washed and pressed in the desired forms. The gun-cotton when finished is usually preserved in a moist state, and dried only when needed for use. It, however, does not require to be sharply dried, as with fifteen to twenty per cent. of moisture it can be made to develop its full explosive powers.

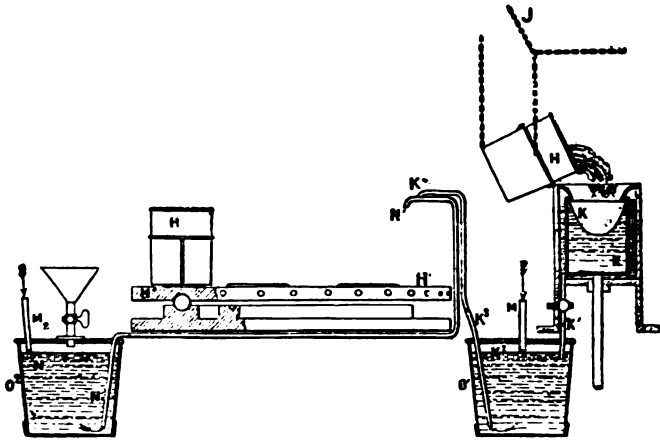
2. Pyroxyline and Collodion.—Pyroxyline of various grades of solubility can be prepared according to the strength of acids used and length of immersion given the cotton. In general, the nitric acid taken is less concentrated than that used for making gun-cotton, and a somewhat higher temperature is employed. Potassium or sodium nitrate is also used along with the sulphuric acid as the nitrating mixture, as the presence of nitrous acid in the nitric acid generated is considered as playing some part in the result. A mixture of twenty parts pulverized potassium nitrate with thirty-one parts of sulphuric acid of 1.835 specific gravity is given as a suitable pyroxyline mixture. After the nitre has entirely dissolved in the sulphuric acid and the mixture has fallen in temperature somewhat below 50° C. the cotton is put in, stirred around thoroughly, and then the vessel left covered for twenty-four hours at a temperature of from 28° to 30° C. The pyroxyline is then washed with cold water until it shows no acid reaction, and finally with boiling water to remove the last traces of potassium sulphate. A similar mixture, using sodium nitrate, is thirty-three parts of sulphuric acid of 1.80 specific gravity, seventeen parts of sodium nitrate, and one-half part cotton.

A special grade of pyroxyline for the manufacture of collodion, put upon the market by the Schering factory in Berlin, is made by immersing cotton for fifteen minutes in a mixture of equal volumes of sulphuric acid of 1.845 specific gravity and nitric acid of 1.40 specific gravity, taken at a temperature of 80° C.

The pyroxyline made from tissue-paper for the celluloid manufacturers is made by taking fifty cubic centimetres of nitric acid of 1.47 specific gravity, one hundred cubic centimetres nitric acid of 1.36 specific gravity, and one hundred cubic centimetres of sulphuric acid of 1.84 specific gravity. In this mixture eighteen grammes of the finely-shredded tissue-paper are immersed at a temperature of 55° C. for one hour. The paper gains about forty per cent. in weight in the nitration.

The method of carrying out this nitration as proposed by Hyatt, the patentee of celluloid, is shown in the annexed illustration. (See Fig. 90.) The shredded paper is filled into the container *H*, in which has been placed a mixture of strong sulphuric and nitric acids heated to from 26° to 32° C. The mixture having been vigorously stirred by a mechanical stirrer which can be raised and lowered at will, it is allowed to remain at rest for twenty minutes to allow of the completion of the nitration. It is then swung around on the revolving table $H^1$, caught by a crane from above, and emptied into the centrifugal *K*, which quickly drains off the excess of acid from the mass, the liquid flowing through the pipe $K^1$ into the reservoir $O^1$. The container *H* can be filled from this reservoir through the pipe $K^3$ by

the application of air pressure at *M*, as the lid of the acid reservoir is fitted on air-tight. $O^2$ is a reservoir for fresh acid mixture.

Fig. 90.

The proportions of ether and alcohol used in dissolving pyroxyline to make collodion solutions vary very greatly. The United States Pharmacopœia prescribes for four parts of pyroxyline seventy parts of stronger ether and twenty-six parts of alcohol; the British Pharmacopœia takes for one ounce of pyroxyline thirty-six fluidounces of ether and twelve fluidounces of rectified spirit; the German Pharmacopœia takes one part of pyroxyline to twenty-one parts of ether and three parts of alcohol.

3. Celluloid.—The conversion of pyroxyline into celluloid is accomplished by effecting a thorough incorporation with the former of a certain amount of camphor. This may, however, be done in a number of ways, several of which have been carried out in practice. First, it is possible to effect it by heat alone, without the use of any solvent for either the camphor or the pyroxyline. The camphor at the temperature of its fusion becomes a sufficient solvent for the pyroxyline to effect complete physical admixture. This process is essentially that used in this country. The weighed amount of camphor is added to the pyroxyline while the latter is still in a partially moist condition, some alcohol sprinkled upon the mixture to aid in the comminution of the camphor, and the materials carefully ground together in closed drums. The mixture may now be put through heated rolls to effect the melting of the camphor and cause it to penetrate and take up the pyroxyline in every part of the mass. It is then put through a heated masticating machine to complete the admixing and make the mass of uniform composition throughout. Coloring matter is added when desired to the materials before the camphor takes up the pyroxyline, so that it may be thoroughly distributed or dissolved as the case may be.

A solution of camphor in either ethyl or methyl alcohol has also been used as the means of converting the pyroxyline into celluloid. This may [illegible]e either with the aid of heat or, if sufficient of the solvent be used, it may [illegible]rried out at ordinary temperatures.

[illegible]olution of camphor in ether has also been used in the celluloid fac[illegible] Magnus & Co. in Berlin. For fifty parts of pyroxyline is taken

twenty-five parts of camphor dissolved in one hundred parts of ether to which five parts of alcohol have been added. The mixture is covered up and stirred from time to time. A gelatinous and glutinous mass results, which must be rolled between calender rolls until it acquires plastic characters. The process is distinctly more dangerous than the others mentioned, as the ether is all allowed to evaporate, and it does not yield anything better in the way of product.

## III. Products.

1. GUN-COTTON.—The explosive variety of gun-cotton, whether in the form of loose fibre or as compressed cartridge or paper sheets, cannot be readily told by outward characteristics from untreated cotton. Microscopically it has not changed. It is on close examination seen to be not quite so white, a slight yellowish tint being recognizable; it is slightly rougher to the touch, and crinkles slightly when pressed; when rubbed it is easily electrified and sticks to the fingers. When lighted it burns quickly without smouldering or leaving any residue. When heated slowly it begins to decompose with evolution of acid fumes, and above 130° C. it explodes. It is therefore necessary to exercise great care in the drying of it, and especially if all traces of acid have not been removed. It is much safer when wet than dry, although it is possible to explode it by concussion when it still contains from fifteen to twenty per cent. of water.

Gun-cotton is insoluble in water, alcohol, ether, chloroform, and acetic acid, in dilute acids and alkalies. It is somewhat soluble in acetone and wood-spirit.

Gun-cotton is chiefly used in submarine mines and blasting and for naval torpedoes. The combination of it with nitro-glycerine, known as blasting gelatine, has been referred to under another section. (See p. 77.)

2. PYROXYLINE.—This in most physical characters resembles perfectly the explosive gun-cotton. The most important difference is the ready solubility of this variety of cellulose nitrate in a mixture of alcohol and ether, in which the true gun-cotton is insoluble. The ordinary pyroxyline is, moreover, only slightly explosive. When dissolved in the strength noted before (see preceding page) we obtain,—

3. COLLODION.—This is a colorless liquid, which rapidly evaporates on exposure to the air, leaving a transparent film of tetranitrate, or tetra- and trinitrate mixed, insoluble in water and alcohol. It is used as a dressing for wounds under the name of "liquid adhesive plaster," and very largely in photography as a means of covering the photographic plates with a transparent film which shall hold finely divided and distributed the sensitive silver salt.

4. PYROXYLINE VARNISHES.—In recent years a very important class of metal varnishes or lacquers have been introduced under trade-names, such as Zapon varnish, etc., in which pyroxyline is the basis. This is dissolved in either methyl alcohol, acetone, methyl and amyl acetates, or mixtures of these. Petroleum-naphtha is also added to these solvents to facilitate the drying. These varnishes are of special value for fine metal-work in brass or bronze, as they leave a perfectly transparent and flexible film of pyroxyline, which protects the metal and will not crack or peel when properly applied.

5. CELLULOID.—This valuable product of the action of camphor upon pyroxyline is prepared under a great variety of forms, both transparent and

opaque, colored uniformly, or mottled and striated in imitation of ivory, coral, amber, tortoise-shell, agate, and other substances. It cannot be caused to explode by heat, friction, or percussion. When brought in contact with flame it burns with a rustling flame, and continues to smoulder after the flame is extinguished, the camphor being distilled off with production of thick smoke, while the nitro-cellulose undergoes incomplete combustion.

Celluloid dissolves in warm, moderately concentrated sulphuric acid, but is carbonized by the strong acid. It is readily soluble in glacial acetic acid, and on diluting the solution with water both camphor and pyroxyline are reprecipitated. It is rapidly soluble in warm, moderately concentrated nitric acid (four volumes of fuming acid to three of water), and is also dissolved with ease by a hot concentrated solution of caustic soda. Ether dissolves out the camphor from celluloid, and wood-spirit behaves similarly. Ether-alcohol (3 : 1) dissolves both the nitro-cellulose and camphor, leaving the coloring and inert matters as a residue. The density of celluloid ranges from 1.310 to 1.393. When heated to 125° C., it becomes plastic and can be moulded into any desired shapes. Separate pieces can also be welded together by simple pressure when at this temperature. The celluloid is easily cemented to wood, leather, etc., by the use of collodion or a solution of shellac and camphor in alcohol.

## IV. Analytical Tests and Methods.

Pure hexanitrate of cellulose will keep indefinitely, but the presence of free acid, of lower nitrates, or of fatty and waxy matters render it more or less unstable, and therefore unsafe. The most important determinations to make are the examination for free acid and for lower nitrates, and the valuation by means of the estimation of $NO_2$ liberated from any sample.

1. Examination for Free Acid.—This may be detected by treating twenty grammes' weight of the gun-cotton with fifty cubic centimetres of cold water. After twelve hours the water may be pressed out, filtered, and twenty-five cubic centimetres titrated with decinormal caustic alkali. With the remainder of the liquid the nature of the acid, whether sulphuric or nitric, may be ascertained by the usual tests.

2. Examination for Lower Nitrates.—These may be detected if present by treating five grammes of the sample, previously dried at 100° C., with one hundred cubic centimetres of a mixture of three parts of ether and one of alcohol. The mixture is shaken frequently during twelve hours, and then rapidly filtered through loosely-packed glass-wool, the filtrate evaporated at a gentle heat, and the residue weighed.

3. Examination for Unaltered Cellulose.—This may be estimated by treating the gun-cotton left undissolved by the ether-alcohol with acetic ether, which dissolves the hexanitrate and leaves the unchanged cotton. An alternative plan is to prepare a solution of sodium stannite by adding caustic soda to a solution of stannous chloride until the precipitate at first formed is just redissolved. This solution when boiled with gun-cotton dissolves the cellulose nitrates without affecting the unchanged cellulose. Sodium sulphide is also used for the same purpose.

4. Valuation by Determination of $NO_2$.—The nitrogen peroxide contained in gun-cotton and similar nitrated products is frequently determined by the aid of the reaction of sulphuric acid and mercury upon the nitrates as carried out in a Lunge's nitrometer. This is a burette provided

at the one end with stopcock and funnel-tube and narrowed at the other end, which is connected by a stout piece of rubber tubing with a simple graduated burette-tube. The burette with the stopcock is filled with mercury through the rubber connection with the other tube and the stopcock closed. .35 gramme of gun-cotton, dissolved in five cubic centimetres of concentrated sulphuric acid, are then put into the funnel-tube, and by opening the stopcock and lowering slightly the connecting burette are drawn into the stoppered tube, washed out of the funnel with a little additional pure sulphuric acid, and the stopcock closed. The tube is then shaken vigorously until the reaction is complete and the volume of gas no longer increases. It is then allowed to attain constant temperature and the volume read off with correction for temperature and pressure. Allen (Commercial Organic Analysis, 2d ed., vol. i. p. 328) recommends that the volume be compared with that yielded by a standard sample or a nitre solution.

## V. Bibliography and Statistics.

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## STATISTICS.

I. *a*. PRODUCTION, CONSUMPTION AND EXPORTATION OF COTTON FROM THE UNITED STATES.

| YEAR. | Production. | Domestic consumption. | Exportations. | Value of exportations. |
|---|---|---|---|---|
| | Pounds. | Pounds. | Pounds. | Dollars. |
| 1894–95 . . . . | 5,036,964,409 | 1,519,431,300 | 3,517,433,109 | 204,900,990 |
| 1895–96 . . . . | 3,592,416,851 | 1,257,190,466 | 2,335,226,385 | 190,056,460 |
| 1896–97 . . . . | 4,397,177,704 | 1,293,422,755 | 3,103,754,949 | 230,890,971 |
| 1897–98 . . . . | 5,677,259,827 | 1,826,995,532 | 3,850,264,295 | 230,442,215 |
| 1898–99 . . . . | 5,794,767,917 | 2,006,848,795 | 3,773,410,293 | 209,564,774 |

(Statistical Abstract, United States Treasury Department.)

I. *b*. WORLD'S SUPPLY AND CONSUMPTION OF COTTON.

(Bales of 500 pounds.)

| | 1894–95. | 1895–96. | 1896–97. | 1897–98. | 1898–99. |
|---|---|---|---|---|---|
| Crop of the United States . . . . . . . | 9,640,000 | 6,912,000 | 8,435,000 | 10,890,000 | 11,189,205 |
| Crop of other countries . . . . . . . . | 1,625,000 | 1,938,000 | 1,924,000 | 1,665,000 | 2,342,464 |
| Total crop. . . . . . . . . . . . . | 11,265,000 | 8,850,000 | 10,359,000 | 12,555,000 | 13,531,669 |
| Consumption in United States . . . . | 2,743,000 | 2,572,000 | 2,738,000 | 3,002,000 | 3,553,000 |
| Consumption in Great Britain . . . . | 3,250,000 | 3,276,000 | 3,224,000 | 3,406,000 | 3,519,000 |
| Consumption on Continent . . . . . . | 4,030,000 | 4,160,000 | 4,368,000 | 4,485,000 | 4,836,000 |
| Consumption in India . . . . . . . . | 1,074,000 | 1,105,000 | 1,004,000 | 1,075,000 | 1,297,000 |
| World's consumption . . . . . . . | 11,097,000 | 11,113,000 | 11,334,000 | 11,968,000 | 13,205,000 |

II. FLAX.—According to a United States consular report from Odessa (United States Consular Reports, March, 1891, p. 365), the total area sown in Europe with flax amounted to 5,700,000 acres, of which Russia alone had 3,700,000 acres. The total quantity of flax fibre produced in Europe is there given as follows:

| | Pounds. | | Pounds. |
|---|---|---|---|
| Russia . . . . . . . . . . | 900,000,000 | Belgium . . . . . . . | 43,200,000 |
| Austria-Hungary . . . . | 104,400,000 | Italy . . . . . . . . . | 43,200,000 |
| Germany . . . . . . . . | 97,200,000 | All other countries . . . | 36,000,000 |
| France . . . . . . . . . . | 79,200,000 | | |
| Ireland . . . . . . . . . . | 46,800,000 | | 1,350,000,000 |

In 1898 the amount of flax fibre produced in Europe was:

| | Pounds. | | Pounds. |
|---|---|---|---|
| Russia | 1,530,776,000 | Netherlands | 12,934,000 |
| Austria-Hungary | 114,097,000 | Sweden | 4,223,000 |
| Italy | 41,917,000 | Servia | 1,237,000 |
| Belgium | 32,246,000 | | |
| France | 25,126,000 | Total | 1,762,556,000 |

III. Jute.—The exportations of jute, etc., from Calcutta and Chittagong in recent years have been:

| Year. | Jute. | Rejections. | Cuttings. | Total. |
|---|---|---|---|---|
| | Bales. | Bales. | Bales. | Bales. |
| 1890–91 | 2,640,821 | 51,459 | 524,250 | 3,216,530 |
| 1891–92 | 1,714,063 | 21,733 | 209,054 | 1,944,480 |
| 1892–93 | 2,549,634 | 40,924 | 411,884 | 3,002,442 |
| 1893–94 | 2,151,344 | 50,151 | 206,102 | 2,407,577 |
| 1894–95 | 2,969,627 | 55,792 | 436,803 | 3,462,222 |

(Textile Manufactures, June 15, 1895.)

IV. Importations of Vegetable Fibres.—The importations of unmanufactured vegetable fibres into the United States during the last few years have been as follows:

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| Flax (tons) | 7,833 | 9,190 | 5,529 | 6,474 |
| Valued at | $1,804,428 | $1,897,976 | $1,193,597 | $1,306,520 |
| Hemp and substitutes (tons) | 55,694 | 51,380 | 54,287 | 57,136 |
| Valued at | $4,674,088 | $4,048,179 | $3,799,675 | $6,688,583 |
| Jute (tons) | 88,992 | 68,550 | 112,306 | 83,161 |
| Valued at | $2,001,206 | $1,640,484 | $2,543,498 | $2,296,189 |
| Sisal-grass, etc. (tons) | 52,130 | 63,266 | 69,322 | 71,898 |
| Valued at | $3,412,760 | $3,834,732 | $5,169,900 | $9,211,377 |

V. Paper and Pulp Statistics.—

*Paper-making Materials.*—The importations of paper stock for the last three years have amounted, according to the United States Bureau of Statistics, to:

| | 1897. | 1898. | 1899. |
|---|---|---|---|
| Rags other than woollen (pounds) | 51,181,009 | 49,800,209 | 55,596,560 |
| Valued at | $668,385 | $699,981 | $805,545 |
| All other stock valued at | $2,403,320 | $2,170,342 | $1,809,369 |
| Wood-pulp (tons) | 41,770 | 29,846 | 33,319 |
| Valued at | $800,886 | $601,642 | $671,506 |

The English importations of paper-making materials during the last three years have been:

| | 1897. | 1898. | 1899. |
|---|---|---|---|
| Linen rags (tons) | 25,333 | 20,559 | 20,617 |
| Valued at | £249,631 | £193,808 | £174,661 |
| Esparto (tons) | 204,579 | 197,341 | 207,604 |
| Valued at | £825,195 | £768,779 | £806,354 |
| Wood-pulp (chemical tons) | 388,304 (chemical and mechanical combined) | 179,510 | 196,926 |
| Valued at | £1,939,761 (chemical and mechanical combined) | £1,226,026 | £1,441,809 |
| Wood-pulp (mechanical tons) | | 225,317 | 218,180 |
| Valued at | | £668,302 | £547,897 |

According to "Bradstreet's" for November 29, 1890, the American output of wood-pulp more than trebled within ten years. There were

then 210 factories engaged in its manufacture,—183 producing it by the mechanical process, 15 by the soda, and 12 by the sulphite methods.

According to a report made to the United States Department of Labor in 1898, there were in the first half of 1898, 723 paper and pulp manufacturers having altogether 1067 mills. Of the 723 manufacturers, 644 reported their production for the half-year, amounting to 994,087 tons of paper and 619,383 tons of pulp. The value of the paper was \$48,689,880, and of the pulp, \$13,428,542; together, \$62,118,422. The States with largest production were Massachusetts, New York, Maine, Wisconsin, and Pennsylvania. Almost one-third of the paper production—viz., 311,898 tons—was used for the daily newspapers. The production of colored paper amounted to 124,339 tons; of wood-fibre Manila paper, 72,073 tons; of cardboard, 70,694 tons; and of Manila papers, 760,383 tons. The 619,383 tons of pulp were made up of 367,744 tons of ground wood-pulp, 173,420 tons of sulphite pulp, 74,379 tons of soda pulp, and 3840 tons of cotton fibre.

Reckoning on the production of this half-year, and counting in the 79 establishments not reporting, the annual production of the United States is estimated at about \$105,000,000 of paper and \$28,500,000 of pulp. The figures in the census year 1890 were \$72,773,093 for paper and \$5,152,038 for pulp.

The total export from Norway of moist machine wood-pulp has been as follows in recent years: In 1889, 190,000 tons; in 1890, 207,000 tons; in 1891, 230,000 tons; in 1892, 215,000 tons; in 1893, 230,000 tons; in 1894, 240,000 tons. The value of the 1894 exportation was from 9,500,000 to 10,000,000 krona (1 krona = \$0.26.8).

The exportation of chemical wood-pulp from Norway was, for 1893, 32,000 tons of dry and 13,000 tons of moist pulp; for 1894, 34,000 tons of dry and 10,000 tons of moist pulp. The value was between 6,000,000 and 6,500,000 krona.

# CHAPTER IX.

## TEXTILE FIBRES OF ANIMAL ORIGIN.

As before stated, the only animal fibres that have acquired technical importance are the wool fibre and silk. These will now be considered.

## I. Raw Materials.

*A.* WOOL.—Wool is undoubtedly a variety of hair, found in greater or less quantity on almost all mammals, on a few of which, as the domestic sheep, it forms the principal covering of the body. It is probable that while both hair and wool occur together in wild sheep, domestication has gradually caused the rank hairy fibres to disappear and the soft under-wool to develop until the fleece of wool becomes a thick and complete covering. From ordinary hair the wool is distinguished by two important properties: First, while hair is almost smooth on the surface, the wool fibre is covered by minute overlapping scales arranged like roof-tiles. While these scales are so minute as not to be discernible to the eye, they can be felt if a woollen fibre is drawn between the fingers in the direction opposite to that in which the scales are set. Secondly, while a hair is perfectly straight, the woollen fibre is finely crimped or curled, so that it becomes longer when drawn out and shortens again when the strain is removed. The spring due to this curled structure gives woollen fabrics notable elasticity. Owing to the overlapping scale-like structure and the crimped condition of the fibre, wool has also the power of felting, or becoming matted into a compact cloth under the fulling process without the necessity of weaving. These structural characters of the wool fibre are shown in Fig. 91.

FIG. 91.

Sheep's wool ($\frac{340}{1}$).

Sheep's wool varies from the long straight coarse hair of certain varieties of the English sheep (Leicester, Lincolnshire, etc.) to the comparatively short wavy fine soft wool of the Spanish and Saxon Electoral sheep. According to the average length of the fibres or staples two principal classes of wool are established, the *long-stapled* (eighteen to twenty-three centimetres) and

the *short-stapled* wools (two and five-tenths to four centimetres). The former class have hitherto been combed and then spun into *worsted* yarn, while the latter have been carded and spun, yielding *woollen* yarns. These processes will be referred to again later. (See p. 314.) In general the long straight wools, like Lincoln and Leicester wools, possess a silky lustre, and are known as *lustre* wools, while the Merino, Colonial, etc., which are shorter and curly, are known as *non-lustre* wools.

The worth of any grade of wool is determined by noting such properties as softness, fineness, length of staple, waviness, lustre, strength, elasticity, flexibility, color, and the facility with which it can be dyed. Wool is very hygroscopic. In warm dry weather it may contain eight to twelve per cent. moisture, but if kept for a time in a damp atmosphere it may take up thirty to fifty per cent. This becomes an important item in the sale of wool, and hence in France and Germany the percentage of moisture contained in wool to be sold must be officially determined in "wool-conditioning" establishments. (See silk-conditioning, p. 311.) The legal amount of moisture allowed on the Continent is 18.25 per cent.

The best kind of wool is colorless, but inferior grades are often yellowish, and sometimes even brown or black in color.

The chemical composition of the wool fibre is, as already noted (see p. 273), nitrogenous, but we must at the same time distinguish between the true fibre and the encrusting matters. These latter, independent of mechanically adhering impurities or "dirt," are of twofold character, the "*wool-fat*" (soluble in ether) and the "*wool-perspiration*" (soluble in water). These two are frequently included together under the name of the "yolk" or "suint" of the wool. The true wool fibre, when cleansed from these, has approximately the following composition: Carbon, 49.25 per cent.; hydrogen, 7.57 per cent.; oxygen, 23.66 per cent.; nitrogen, 15.86 per cent.; sulphur, 3.66 per cent. The presence of sulphur is very distinctive of wool and serves to distinguish it from silk, the other nitrogenous fibre. It can be removed in large part, but not without weakening the fibre and destroying its lustre, etc.

Wool-fat is a mixture of a solid alcoholic body, cholesterine, together with isocholesterine and the compounds of these bodies with several of the fatty acids. These free higher alcohols are soluble in boiling ethyl alcohol, while the compounds they form with the fatty acids are insoluble in alcohol but soluble in ether.

Wool-perspiration has been shown to consist essentially of the potassium salts of oleic and stearic acids, possibly other fixed fatty acids, also potassium salts of volatile acids, like acetic and valerianic acid, and small quantities of chlorides, phosphates, and sulphates. The wash-water of raw or greasy wool, it will be seen, therefore, would contain large amounts of potash salts, and when evaporated and ignited would yield an abundant product of potassium carbonate. This utilization of the wool wash-water as carried out at present in France and Belgium yields over one million kilos. of potassium carbonate. Another utilization of this yolk of wool is to submit it to dry distillation, when it yields a residue which is an extremely intimate mixture of carbonate of potash and nitrogenous carbon, of great value for the manufacture of yellow prussiate of potash.

Wool is decomposed by heat at 130° C., ammoniacal vapors are given [illegible] and at 140° to 150° C. sulphur compounds are also present in the [illegible]s. When ignited by a flame, wool emits the disagreeable odor of

burnt feathers and leaves a porous caked residue. Ammoniacal solution of cupric hydrate has no action upon wool in the cold, but dissolves it when hot. Dilute solutions of hydrochloric and sulphuric acids have little influence whether hot or cold. This fact is availed of in separating cotton from wool in the process of "carbonizing" mixed cotton and woollen goods. The dilute sulphuric acid used attacks and disintegrates the cotton. They are then dried in closed chambers at 110° C., after which the disorganized cotton can be beaten out, while the wool remains but slightly altered. Nitric acid does not attack the wool seriously, but gives it a yellow color, hence sometimes used as a "stripping" agent for dyed woollen goods in case of re-dying. Sulphurous acid is the most satisfactory bleaching agent for woollens, as it removes the natural yellow tint of the ordinary wool. Caustic alkalies act rapidly and injuriously upon wool. Alkaline carbonates and soap have little or no injurious action if not too concentrated and if the temperature is not above 50° C. Chlorine and hypochlorites act injuriously upon wool and cannot be used for bleaching. A very slight action of chlorine, on the other hand, causes wool to assume a yellowish tint and gives it an increased affinity for many coloring matters.

Closely related to sheep's wool are a few varieties of animal hair, which are also utilized in some degree as textile fibres in similar classes of goods.

*Mohair* is the product of the Angora goat of Asia Minor and Cape Colony, South Africa. It is a long silky hair, which is very soft and lustrous.

*Cashmere* consists of the soft under-wool which grows in winter on the Cashmere goat. It furnishes the material for the costly Cashmere shawls of native manufacture, but is not exported at all as fibre.

*Alpaca, Vicuna, Llama,* and *Guanaco* are the names of four closely-related species of South American goats found on the western slopes of the Andes, which yield valuable hair-like fibres. Of these, the alpaca is exported in largest amount to Europe and the United States. It is a long silky fibre somewhat intermediate between true wool and hair and possessing a strong lustre. It is both white and of various colors. It is shown in Fig. 92.

FIG. 92.

Alpaca goat's hair ($\frac{340}{1}$).

*Camel's Hair* is somewhat used in Africa, Asia Minor, and the Caucasus, and latterly in Europe, for the manufacture of woven goods, which are made from the unbleached hair.

*B.* SILK.—The silk fibre is, morphologically, the simplest and at the same time, because of its properties, the most perfect of the textile fibres. It differs from all other fibres in that it is found in nature as a continuous fine thread, so that the process of spinning is superfluous in its case. In place of this we have the reeling process, whereby several of the natural threads are united into one thicker and stronger thread.

Silk is the product of the silk-worm (*Bombyx mori*) and is simply the fibre which the worm spins around itself for protection when entering the pupa or chrysalis state. From the eggs laid by the animal in the moth or butterfly state develops the cater-

pillar or silk-worm. The eggs are yellowish in color at first, changing to gray when dry. They are very light in weight, some thirteen hundred and fifty together weighing one gramme. For the development of the caterpillar from them a certain amount of warmth and moisture is necessary, the temperature being raised in the incubation chamber during ten or twelve days from 18° to 25° C. The young worms are at once removed to larger chambers, where are lath frame-works strung across with threads and sheets of paper. The animals are placed upon these, and fed regularly during thirty to thirty-three days, till indeed they begin to spin. They are here fed upon mulberry leaves (*Morus alba*), and during this period increase enormously in size, becoming at length about eight to ten centimetres long and about five grammes in weight. To allow of this increase in size it casts its skin some four times during this period (at intervals of from four to six days). When about the thirtieth day of its growth has been reached it ceases to take food and shows a decided restlessness. It is then placed on birch-twigs, and soon begins to spin. This spinning of the cocoon, or oval-shaped house in which the worm is to undergo the chrysalis state before emerging as the butterfly, involves the secretion of the fibre so much prized as silk. The silk substance is secreted by two glands, one on either side of the body of the caterpillar. The substance from these two glands unites in a capillary canal situated in the head of the animal, whence issues the silk as a double fibre only

Fig. 94.

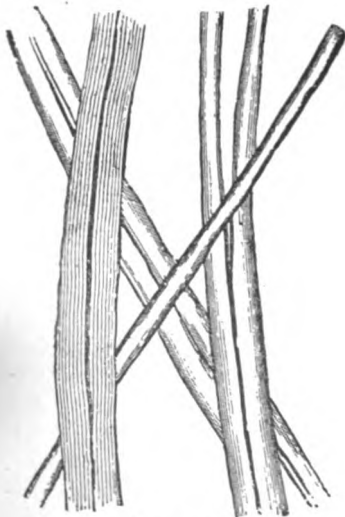
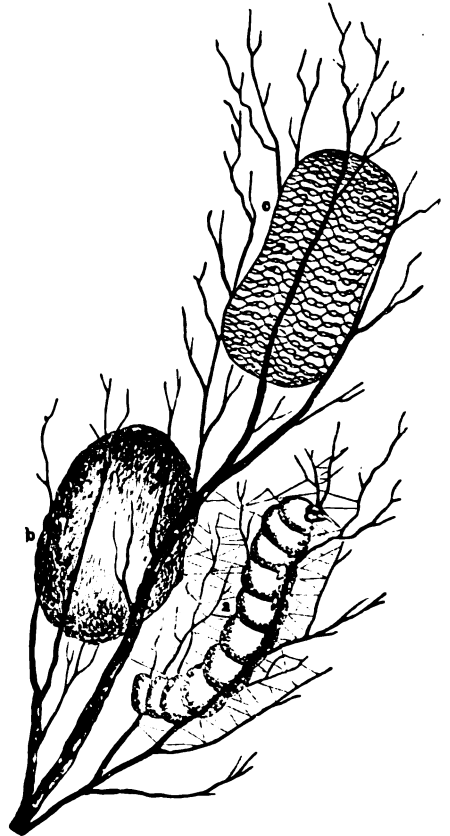



Fig. 93.

Silk fibre ($\frac{350}{1}$).

rarely separated, cemented throughout by the sericin, or silk-glue. The microscopical appearance of the silk fibre is shown in Fig. 93. This fibre

which goes to form the cocoon varies in length from three hundred and fifty to twelve hundred and fifty metres, and with a diameter of about .018 millimetre in diameter. The interlacing layers of the silk cocoon are at first loose, but become finer and denser towards the interior, while the innermost layer which immediately surrounds the animal forms a thin parchment-like skin. The several stages of cocoon-spinning are shown in Fig. 94. The cocoons of the female are pure oval in shape, while those of the male are distinctly contracted in the centre. They are white or yellowish, and usually about three centimetres long and one and one-half to two centimetres thick. Some seven or eight days are allowed for the completion of the cocoon-spinning, and they are then gathered. A sufficient number of both males and females are taken for breeding purposes, and the rest put aside to be reeled for silk. Those chosen for breeding are kept for some twenty days at a temperature of from 19° to 20° C., when the silk-moth which has formed in the interior from the pupa emits a peculiar saliva, which softens the sericin, or silk-glue, at one end of the cocoon and enables the animal to push its way out to daylight. The females within forty hours after their appearance lay their eggs, some four hundred in number, and shortly after die. The eggs are slowly dried, and stored in glass bottles in a dry dark place till the following spring. The cocoons put aside for the reeling of silk must be taken in hand promptly and the chrysalis contained in them killed, in order to prevent the development of the silk-moth and the injury to the cocoon by its pushing its way out. This is done either by heating them for several hours in an oven at 60° to 70° C., or more quickly by steam heat. One hundred grammes of eggs produce under favorable conditions from ninety thousand to one hundred and seventeen thousand cocoons, weighing one hundred and fifty to two hundred kilos., and these yield twelve to sixteen kilos. of reeled silk.

The silk fibre consists to the extent of rather more than half its weight of *fibröin*, $C_{15}H_{23}N_5O_6$, a nitrogenous principle. Covering this is the silk-glue, or *sericin*, $C_{15}H_{25}N_5O_8$. Whether this latter exists in the glands of the silk-worm along with the fibröin, as maintained by Duseigneur-Kleber, or is produced exclusively by atmospheric change from the fibröin as asserted by Bolley, is still in debate. This sericin, however, is easily dissolved off from the fibröin by warm soap-water and other alkaline liquids. This "boiled-off" liquid plays an important part in silk-dyeing operations. (See p. 491.) The most important physical properties of the silk fibre are its lustre, strength, and avidity for moisture. The regulation of the amount of moisture contained in raw silk as offered for sale, or "silk-conditioning," will be spoken of under the process of treatment. (See p. 311.)

Besides the true silk, the product of *Bombyx mori*, we have several so-called "wild silks," the most important of which is the Tussur silk, the product of the larva of the moth *Antheræa mylitta*, found in India. The cocoons are much larger than those of the true silk-worm, egg-shaped, and of a silvery drab color. They are also attached to the twigs of the food trees by a thread-like prolongation of the cocoon. The cocoon is very firm and hard, and the silk is of a drab color. It is used for the buff-colored Indian silks, and latterly largely in the manufacture of silk plush. Other wild silks are the *Eria* silk of India, the *Muga* silk of Assam, the *Atlas* or *Fagara* silk of China, and the *Yama-mai* silk of Japan.

## II. Processes of Manufacture.

It will be beyond the province of this work to take up the manufacture of woollen and silk goods from the mechanical side. Hence we shall only notice the preliminary processes of chemical treatment which the fibres undergo to prepare them for manufacture into goods, and then take up the several classes of manufactured textiles again in speaking of bleaching and dyeing of goods.

*A.* WOOL.—1. *Wool-scouring.*—The condition of the raw wool when first obtained from the back of the sheep has already been referred to. The fibre is covered with both natural and artificial impurities (yolk, dirt, etc.) to such an extent that mordanting and dyeing would be almost impossible. These are therefore to be removed by the process of scouring. It will be remembered, too, that the yolk was stated to be made up of the wool-fat (soluble in alcohol) and the wool-perspiration (soluble in water). Both of these have to be removed in the completed scouring operation. The full operation then must include three stages,—viz., steeping, or washing with water (*désuintage*); cleansing or scouring proper with weak alkaline solutions (*dégraissage*); rinsing or final washing with water (*rinçage*). The first operation may be omitted if the wool has been washed by the wool-grower. This is true, for instance, with Australian wools, while, on the other hand, most South American wools come into commerce unwashed and very rich in yolk. The washing of these wools is largely carried on in France and Belgium, and, as has been stated (see p. 306), is made to yield large amounts of potassium carbonate by evaporating and igniting the wash-waters. The wool is systematically washed in tepid water (about 45° C.) in a series of tanks arranged so that the water passes from one to the other until completely saturated, when it is evaporated. According to M. Chandelon, one thousand kilos. of raw wool may furnish three hundred and thirteen litres of yolk solution of specific gravity 1.25 (50° Tw.), having a value of fifteen shillings and sixpence, while the cost of extraction does not exceed two shillings and sixpence.

The scouring and washing processes for loose wool are usually carried out in the well-known rake scouring-machines, consisting of a large cast-iron trough provided with an ingenious system of forks or rakes whereby the wool is gradually passed forward by the to-and-fro digging motion of the rakes. Two or three such scouring-machines are placed in series, so that the first may take the bulk of the impurities, the second complete the scouring, and the third effect a thorough washing in a stream of fresh water. The scouring liquid which has been longest in use is stale urine (*lant*), which is effective because of the ammonium carbonate it contains. It is now largely supplanted by ammonia, sodium carbonate, soaps, etc. The most injurious effects arise from the use of water containing lime or magnesia, because of the formation of the insoluble lime or magnesia compounds upon the fibre. In recent years volatile solvents, like fusel oil, ether, petroleum-naphtha, carbon disulphide, have also been introduced for scouring purposes, although not generally adopted on account of the expense and risk attending their use. They must be followed at all events by a washing with water, as, while they dissolve fatty matters, they do not take up the oleates, etc., of the wool-perspiration.

The only treatment of this kind, known technically as a *degreasing*

process, is that with petroleum-naphtha. This has been found practicable and remunerative. The wool, freed from its grease and wax-like constituents by the naphtha and its potash salts, by a washing with water only is left in an excellent condition for the mechanical treatment, such as carding and combing.

Woollen yarns and woollen cloth are also scoured to free them from the oil which has either purposely or by accident been put upon them in the spinning and weaving operations. The scouring of "union" goods—that is, materials with cotton warp and woollen weft—is a more difficult operation on account of the differences in elasticity, hygroscopic character, etc., of the cotton and the wool fibre. It includes the operations of *crabbing, steaming*, and *scouring*.

2. *Bleaching of Wool.*—Wool is generally bleached either as yarn or cloth. The bleaching agent in general use is sulphur dioxide. It may of course be applied either as gas or as sulphurous acid solution, the former method being generally followed, and the yarn or cloth suspended on poles in closed chambers, called sulphur-stoves, which can be charged with the gas. In liquid bleaching with sulphurous acid, a solution of sodium bisulphite is generally used, which is either mixed with an equivalent amount of hydrochloric acid or, what is better, the goods are passed through one solution after the other in separate baths. The bleaching of sulphur dioxide differs essentially from that effected by chlorine and hypochlorites in that it is not due to oxidation, but to reduction or possibly to the formation of colorless compounds with the natural yellow color of the wool. At all events, it is not permanent in character, and the yellow color gradually returns on exposure to atmospheric influences and repeated washings in alkaline solutions.

The best liquid bleaching agent is hydrogen dioxide. The woollen material is steeped for several hours in a dilute and slightly alkaline solution of the commercial $H_2O_2$ and then well washed, first with water acidified with sulphuric acid and afterwards with pure water.

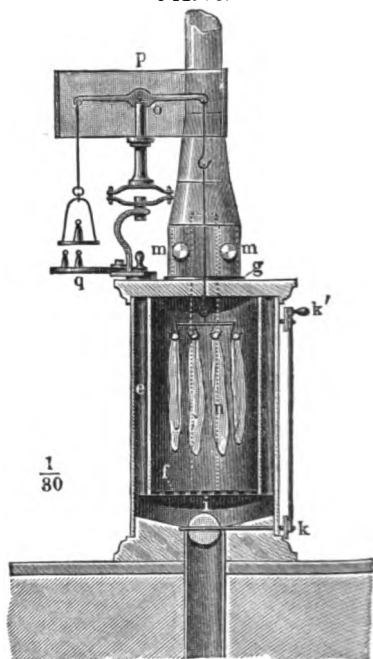
*B.* SILK.—1. *Reeling of Silk.*—The unwinding of the long silk fibre from the cocoon and bringing it into condition for weaving is to be accomplished in the reeling process. The cocoons are thrown into a basin of warm water to soften the silk-glue and allow of the fibres being separated. From four to eighteen fibres, according to the quality, are taken, and two threads formed by passing the fibres together through two perforated agate guides. After being crossed or twisted together at a given point they are again separated and passed through a second pair of guides, thence through the distributing guides on to the reel. The temporary twisting or crossing causes the agglutination of the individual fibres of each thread. In order to form long threads a frequent adding on the fibre of a new cocoon is necessary. Care must be taken, also, that the thread remain as nearly as possible of uniform thickness, so that as the inner fine fibres of several cocoons come through the guides another cocoon is added to the number used for the thread. One cocoon gives .16 to .20 or at most .25 gramme of raw silk. The loss through removal of the external floss varies from eighteen to thirty per cent., according to the cocoons and the care bestowed by the worker. Before this raw silk can be used for weaving two of the threads are "thrown" together and slightly twisted.

2. *Silk-conditioning.*—Raw silk kept in a humid atmosphere is capable of absorbing thirty per cent. of its weight of moisture without this being at all perceptible. It therefore becomes a matter of great importance for

the buyer to know what weight of normal silk there is in any given lot. To ascertain this with accuracy, there have been established in a number of the European centres of silk industry *conditioning* establishments. The operation is carried out by means of the apparatus shown in Fig. 95, where a number of hanks of silk are shown in the drying chamber. A test hank of silk is taken from the bale, and having been suspended from the one arm of an accurate balance its initial weight is gotten. It is then dried in a current of air at 110° C. until constant weight is again obtained. The arrangement of the drying chamber is shown in the illustration. To the final weight obtained for the dry silk eleven per cent. is added, and the result taken as a normal silk weight. The average loss of weight in this conditioning process is about twelve per cent.

Fig. 95.

3. *Silk-scouring.*—By the scouring of silk the silk-glue is removed to a greater or less extent and the fibre is rendered lustrous and soft and able to take the dye-color. According to the amount of silk-glue removed in this operation the product is called *boiled-off silk, souple silk,* or *écru.* In the first case, the loss of silk-glue amounts to twenty-five to thirty per cent. of the weight of the raw silk; in the second, to eight to twelve per cent.; and in the third to three to four per cent. of the original weight of the silk. In preparing the first variety two operations are necessary, *stripping* or *ungumming* (*dégommage*) and *boiling off.*

The hanks of raw silk are suspended by wooden rods in a rectangular trough lined with copper and worked by hand in a thirty to thirty-five per cent. soap solution heated to 90° to 95° C. When the water is very hard it must be corrected or softened previously. Frequently two soap-baths are used one after the other as the first one becomes charged with the silk-glue. The silk at first swells up and becomes glutinous, but as the glue dissolves off it becomes soft and silky. The waste soapy and glutinous liquid obtained is called "boiled-off" liquor, and is a useful addition to the dye-bath in dyeing with coal-tar colors. (See p. 491.) For the purpose of removing the last portions of the silk-glue, it is now washed in water at 60° C., to which some soap and carbonate of soda have been added, then put in coarse hempen bags called "pockets" and boiled for half an hour to three hours, according to quality, in open copper vessels with a solution of ten to fifteen per cent. of soap. It is then rinsed with a weak tepid solution of sodium carbonate, and finally washed in cold water. Silk intended to remain white or to be dyed pale colors is then at once bleached while moist with gaseous sulphur dioxide for some six hours. The bleaching operation may be repeated from two to three times, according to the quality of the silk.

Souple silk is that which has been prepared for dyeing with a loss of not more than eight per cent. of its weight. It is, however, not so strong as boiled-off silk, and is used only for tram. Its preparation always includes two operations, and if the silk is to be dyed light colors, two additional operations have to be carried out. The raw silk is first "softened," and the small quantity of fatty matter present removed (*dégraissage*) by working it from one to two hours in a ten per cent. soap solution at 25° to 35° C. It is then "bleached" by immersion for ten to fifteen minutes in a dilute solution of aqua regia (five parts hydrochloric acid to one part nitric), or as a substitute for this nitrated sulphuric acid (nitrosyl-sulphate). This is followed by "stoving," or treatment with sulphur dioxide, and then, without removing the sulphurous acid, by the treatment of soupling (*assouplissage*) proper. This consists in working the silk for about an hour and a half at 90° to 100° C. in water containing three to four grammes cream of tartar to the litre. This treatment makes the silk softer and causes it to swell up and become more absorbent. It is then finally washed in tepid water.

Écru silk is raw silk which has been washed with hot water, with or without soap, bleached with sulphur, and again washed. It is only used for a base for other silk fabrics like velvet or dyed in blacks.

*B.* 1. Artificial Silk.—In 1888 Chardonnet first brought to the attention of the textile trade a product obtained from cotton by a peculiar treatment, to which the name of "artificial silk" was given, because of its similarity in lustre and general appearance and its capability of readily taking all shades of color when dyed, and of being woven into fabrics as beautiful if not quite as strong and durable as the natural product of the silk-worm. This product is now manufactured on a large scale at Besançon in France, in Belgium, and in Germany, and has become an article of commerce.

The raw material is cotton lint carded into wadding. This is transformed into nitro-cellulose by immersion in a mixture of fifteen parts of nitric acid of 1.52 specific gravity and eighty-five parts of commercial sulphuric acid. The immersion continues until a sample on examination under the microscope with polarized light shows a clear blue color only. The nitrated cotton is then pressed, to free it from excess of acid, and washed until the last trace of acid is removed. After compression, it is taken with thirty-three per cent. of moisture still remaining and dissolved by digestion in autoclaves in a mixture of equal parts of ninety-five per cent. alcohol and ether. The solution after filtering through lint cotton is set aside to "age" or allow of the completion of the chemical change. Finally the solution is put in steel cylinders and under a pressure of from forty to fifty atmospheres is driven through fine glass tubes with minute apertures into water acidulated with one-half of one per cent. of nitric acid and thence wound directly upon bobbins. The skeins are then dried rapidly by a current of warm air at 45° C. and denitrated with a bath of an alkaline sulphide. After thorough washing and drying it is ready for treatment like common silk, taking the basic aniline dyes very readily.

Other processes for the manufacture of analogous "artificial silk" fibres from cotton use ammoniacal cupric hydrate solution and zinc chloride. Cross and Bevan have also prepared a similar artificial and lustrous fibre from their cellulose xanthogenate or viscose product.

## III. Products.

*A*. WOOL.—We have already alluded to the distinction between worsted and woollen yarns. Formerly all long-stapled wools were *combed*,—that is, the fibres were brought as nearly as possible parallel to one another and were then spun into what was known as worsted yarn, used in hosiery and in the manufacture of fabrics which did not undergo fulling. All short-stapled wools, on the other hand, were *carded* and spun much as cotton is spun, and the yarns so obtained were the only ones capable of being used in making milled or fulled cloths, in which the felting property of wool is availed of to thicken the cloth after weaving and in which by teasels the nap of the cloth is raised so as to present a uniform surface. All kinds of wool, therefore, were formerly divided into combing and carding or clothing wools. Machines have been invented latterly, however, capable of combing wools having as short a staple as one inch, and, on the other hand, wools with a staple as much as five inches long may be used in making milled cloth. So the distinction between the several wools is no longer as absolute as it once was.

Among the chief kinds of worsted fabrics are *serges* and *merinos* and mixed goods of wool and mohair, alpaca, and camel's hair. *Hosiery* and *carpets* also belong here, although the best of these latter are made on a ground of strong linen or hemp. The principal varieties of woollen cloth are *broadcloths*, the finest variety of woollen cloth, *cashmeres*, a fine thin twilled fabric, *tweeds*, fabrics of looser texture than broadcloth and less highly milled, *doeskin*, a strong twilled cloth, *blankets*, *flannels*, etc.

*Shoddy* is a material made from fragments of cast-off woollen clothing torn into fibres and re-spun into yarn. It is looser in texture than *mungo*, which is made from remains of finer fragments, such as old dress-coats, tailor's clippings, etc.

A third grade of recovered wool, sometimes called *extract wool*, is obtained from union goods (mixed woollen and cotton goods) by the process of carbonizing the vegetable fibre and then beating it out. The carbonizing is done with dilute sulphuric acid, with aluminum chloride, or with gaseous hydrochloric acid. The last process is said to give the best results.

*B*. SILK.—The raw-silk threads obtained in the reeling process are not sufficiently strong for use in the loom, so several must be united. This may be done in different ways. By the union of two or more single threads, separately twisted in the same direction, which are then doubled and retwisted in the opposite direction, is obtained *organzine*. The best grades of silk are also taken for the organzine, which is to form the warp in silk-weaving. The product of the union of two or more simple untwisted threads which are then doubled and singly twisted is *tram*, which forms the weft in weaving.

*Waste silk* is that which proceeds from perforated and double cocoons and such as are soiled in steaming or in any other way. This waste silk is washed, boiled with soap, and dried. When carded and spun like cotton it yields the so-called *flurt-silk*.

*Satins* are tissues so woven that almost the only threads appearing on the right side of the tissue are weft threads, which present a uniform glossy surface.

*Velvets* are tissues in which the outer surface presents to view a short soft pile, made by passing the warp threads over fine wires, which are after-

wards drawn out. The loops then remaining are either left as they are, in which case the tissue is called *pile-velvet*, or cut to form *cut-velvet*. This fabric is now largely imitated in cotton and mixed tissues.

## IV. Analytical Tests and Methods.

1. GENERAL DISTINCTIONS BETWEEN VEGETABLE AND ANIMAL FIBRES.—A general scheme for distinguishing between the several classes of fibres has been proposed by R. Schlesinger in his "Leitfaden für die mikroskopische und mikrochemische Analyse der technisch verwendeten Rohstoffe der Textil-Industrie." It is in outline as follows:

| TREAT WITH CAUSTIC SODA. | | |
|---|---|---|
| The fibre does not dissolve in ten per cent. caustic soda solution, and in burning, which takes place readily, does not develop any burnt horn odor. | The fibre dissolves in concentrated caustic soda, and when treated with ammoniacal cupric oxide shows scales upon its surface. | The fibre does not dissolve in cold ten per cent. caustic soda, but dissolves perfectly in concentrated sulphuric acid; shows neither scales nor medullary substance. |
| Vegetable fibres. | Animal hairs or wool. | Silks. |

The vegetable fibres are then to be studied by the aid of the iodine and dilute sulphuric acid reaction, and the several groups already noted in the classification on p. 263 are established.

The animal hairs are to be distinguished best by the microscopical characters and measurements.

The several varieties of silk are also to be distinguished by a comparison of the diameters of the fibre as measured under the microscope.

A scheme for distinguishing between the more important textile fibres, based upon their behavior to the two dyes malachite-green and Congo-red, and after examination under the microscope, has been proposed by Behrens ("Microchemische Analyse," 2te Heft, p. 51). The grouping thus established is as follows:

Group A. *Dyed fast to washing by malachite-green.*
Here belong, of the textile fibres, silk, wool, and jute.
Aa. Not capable of supplementary dyeing by aromatic amines: silk and wool.
Ab. Capable of supplementary dyeing by aromatic amines: jute.

Group B. *Dyed partially fast only by malachite-green.*
Hemp and manila.
Ba. Strongly polarizing: hemp.
Bb. Weak polarizing: manila.

Group C. *Fugitive dyeing with malachite-green; complete supplementary dyeing with benzidine dyes.*
Here belong cotton and flax.
Ca. Weak polarizing: cotton.
Cb. Strongly polarizing: flax.

Several of the simpler differences between the vegetable and the animal fibres as groups have already been alluded to in classifying the fibres. (See p. 273.) Other special tests are as follows:

1. Millon's reagent (mercurous and mercuric nitrate) colors the animal fibres red, but not the vegetable fibres.

2. Liebermann gives the following test: Prepare a fuchsine solution, add potash solution drop by drop until it is decolorized, filter, and dip in the sample of goods. Wool or silk fibres are colored red, cotton remains colorless.

3. Ammoniacal cupric oxide solution dissolves cotton as well as silk. While cotton, however, is precipitated by certain salts as well as by sugar and gum, silk is only precipitable by acids.

4. As wool always contains sulphur, a sodium plumbate solution (made by boiling red lead with caustic soda solution and filtering) is at once blackened on contact with wool. This test may be interfered with in the presence of sulphur-treated silk.

5. Wool and silk may be distinguished by the use of hot hydrochloric acid. Silk dissolves easily in this, while wool merely swells up but does not dissolve.

6. According to Höhnel, wild silks behave differently from true silks with chromic acid. If a cold saturated solution of chromic acid be diluted with an equal bulk of water and then boiled for one minute with the sample of silk, the true silk dissolves up, while the wild silk remains unattacked even after two to three minutes' boiling. Wool behaves like true silk in this.

A. Remont gives a process for determining wool, silk, and cotton when mixed in the same fabric. Four pieces of about two grammes' weight each are taken; three of these are boiled for a quarter of an hour in two hundred cubic centimetres of three per cent. hydrochloric acid, which is renewed if the liquid becomes strongly colored, and the samples are then well washed. The dressing is thus removed and the coloring matter in the case of the cotton, but only slightly in the case of wool and silk; the weighting of the silk with iron salts is also completely removed by the hydrochloric acid if the weighting does not exceed twenty-five per cent. of the weight of the silk, leaving the fibres chestnut-brown in color. Two of the samples thus treated are dipped for one to two minutes into a boiling solution of basic chloride of zinc of specific gravity 1.69; then thrown into water and washed first with acidified water and then with pure water. This removes the silk. The basic chloride of zinc solution is prepared by heating one thousand parts of zinc chloride, forty parts of zinc oxide, and eight hundred and fifty parts of water.

One of the two samples freed from silk is then boiled gently for a quarter of an hour with sixty to eighty cubic centimetres of caustic soda solution of specific gravity 1.02. This is best done with inverted condenser, so that an injurious concentration of the soda solution is avoided. Wash gently without too much rubbing and the wool is removed. All four samples are now washed for a quarter of an hour with distilled water, pressed out, dried in the air, and weighed. The first will weigh as before, two grammes or nearly, a slight difference of a few milligrammes being neglected; the difference in weight between the first and second samples gives the dressing; that between the second and third gives the silk; that between the third and fourth the wool present, and the weight of the fourth sample the vegetable fibre present. This is slightly attacked by the soda solution, and in the case of cotton it is usual to reckon five per cent. as the loss from this cause.

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## STATISTICS.

*Wool.*—The following figures show the production, importation, and home consumption of wool for the United States in recent years:

| Year. | Production. | Imports. | Total production and imports. | Home consumption. | Percentage imported. |
|---|---|---|---|---|---|
| | Pounds. | Pounds. | Pounds. | Pounds. | |
| 1895 . . . | 309,748,000 | 206,033,906 | 515,781,906 | 509,159,716 | 40.0 |
| 1896 . . . | 272,474,708 | 230,911,473 | 503,386,181 | 490,413,964 | 45.9 |
| 1897 . . . | 259,153,251 | 350,852,026 | 610,005,277 | 601,305,908 | 57.8 |
| 1898 . . . | 266,720,684 | 132,795,202 | 399,515,886 | 396,889,915 | 32.8 |
| 1899 . . . | 272,191,330 | 76,736,209 | 348,927,539 | 334,832,204 | 19.2 |

The importations of wool during the last few years are thus classified:

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| Class I.—Clothing wool (lbs.) . . | 117,233,440 | 200,759,079 | 45,442,987 | 12,976,999 |
| Valued at . . . . . . . . | $19,448,471 | $34,281,656 | $7,969,611 | $1,948,954 |
| Class II.—Combing wool (lbs.) . | 15,756,318 | 37,951,490 | 4,320,873 | 2,155,419 |
| Valued at . . . . . . | $3,509,736 | $7,187,620 | $859,599 | $587,061 |
| Class III.—Combing wool (lbs.) . | 97,921,715 | 112,141,457 | 83,031,342 | 61,603,791 |
| Valued at . . . . . . . . . | $9,493,035 | $11,773,915 | $7,954,482 | $5,786,882 |

The "wool book" of the National Association of Wool Manufacturers gives the following as the world's production for 1891:

| | Pounds. |
|---|---|
| Europe: | |
| Russia . . . . . . . . . . | 291,500,000 |
| Great Britain and Ireland . | 147,475,000 |
| France . . . . . . . . . | 124,803,000 |
| Spain . . . . . . . . . . | 66,138,000 |
| Germany . . . . . . . . | 54,894,000 |
| Hungary . . . . . . . . | 43,146,000 |
| Austria . . . . . . . . . | 11,155,000 |
| Italy . . . . . . . . . | 21,385,000 |
| Portugal . . . . . . . . . | 10,362,000 |
| Belgium . . . . . . . . . | 4,409,000 |
| Sweden . . . . . . . . | 3,307,000 |
| All other Europe . . . . . | 8,818,000 |
| Total Europe . . . . . | 787,392,000 |
| North America: | |
| United States . . . . . . . | 307,100,000 |
| British provinces . . . . . | 12,000,000 |
| Total North America . | 319,100,000 |
| South America: | |
| Argentine Republic . . . . | 376,700,000 |
| Brazil . . . . . . . . . . | 1,875,000 |
| Peru . . . . . . . . | 6,700,000 |
| Uruguay . . . . . . . . . | 42,000,000 |
| Total South America . | 427,275,000 |
| Australasia . . . . . . . . . | 550,000,000 |

| Asia: | Pounds. |
|---|---|
| British East Indies | 72,000,000 |
| Russia | 66,000,000 |
| Asiatic Turkey, Persia, Thibet, Afghanistan, etc. | 12,200,000 |
| Sivas, Asiatic Turkey | 8,300,000 |
| Mesopotamia | 31,555,000 |
| Persia | 3,470,000 |
| Total Asia | 193,525,000 |

| Africa: | Pounds. |
|---|---|
| Cape Colony, Natal, | 128,681,600 |
| Egypt | 2,800,000 |
| Total Africa | 131,481,600 |
| All other countries | 48,000,000 |
| Total production | 2,456,773,600 |

The wool clip of the principal fine wool-producing countries for 1894 is given as follows:

| | | |
|---|---|---|
| United States | 325,000,000 | pounds. |
| Australasia | 581,000,000 | " |
| Cape of Good Hope | 122,000,000 | " |
| River Platte | 443,000,000 | " |
| Total | 1,471,000,000 | " |

(Textile Manufacturer, June 15, 1895.)

The entire wool clip for 1894 is estimated to have been 2,692,000,000 pounds.

The following statistics of the Australian wool export are given in the United States Consular Reports of June, 1890:

| | 1888–89. Bales. | 1889–90. Bales. |
|---|---|---|
| Victoria | 336,702 | 400,459 |
| New South Wales | 422,863 | 443,820 |
| Queensland | 87,763 | 85,206 |
| South Australia | 118,656 | 143,215 |
| West Australia | 21,170 | 24,337 |
| Tasmania | 19,536 | 19,251 |
| New Zealand | 207,023 | 210,265 |
| | 1,215,712 | 1,326,643 |

The value of the clip in 1889–90 is placed at £21,253,188, or $103,-428,639.

The number of sheep in the United States in 1891 is stated by the Department of Agriculture to have been 43,430,000.

The number of sheep in the Argentine Republic for the year 1887 is given as 103,413,817.

The number of sheep in all the Australian colonies in 1891 is reported to have been 114,628,301.

The "wool book" for 1892 gives the following comparison of the quantities of wool manufactured in the United States, England, France, and Germany at the dates stated:

| | 1866. | 1876. | 1884. | 1890. |
|---|---|---|---|---|
| | Pounds. | Pounds. | Pounds. | Pounds. |
| United States (imported and home grown) | 229,707,000 | 235,020,000 | 376,036,000 | 415,000,000 |
| United Kingdom (imported and home grown) | 313,000,000 | 369,000,000 | 381,000,000 | 470,000,000 |
| France | *190,119,000 | *271,484,000 | *365,767,000 | 420,000,000 |
| Germany | no returns. | *143,260,000 | *232,962,000 | 340,000,000 |

* Home grown not included.

*Silk.*—The statistics for the production of raw silk for the year 1890 throughout the world are thus given in Dammer's "Handbuch der Chemischen Technologie," Bd. v. p. 30:

| *Europe:* | |
|---|---|
| Italy | 3,448,000 kilos. |
| France | 650,000 " |
| Austria-Hungary | 245,000 " |
| Balkan States | 154,000 " |
| Spain | 84,000 " |
| Switzerland | 40,000 " |
| Portugal, etc. | 4,000 " |
| Total | 4,620,000 " |

| *Asia:* | |
|---|---|
| China | 11,000,000 kilos. |
| Japan | 6,000,000 " |
| East Indies | 1,500,000 " |
| Asiatic Russia | 656,000 " |
| Syria, Asia Minor | 571,000 " |
| Persia | 275,000 " |
| Farther India | 270,000 " |
| Miscellaneous | 100,000 " |
| Total | 20,372,000 " |

The exports of raw silk from different Asiatic ports during the last two years have been as follows:

| | 1898. Kilos. | 1899. Kilos. |
|---|---|---|
| Persia and Turkestan | 133,000 | 240,000 |
| China (Shanghai and Canton) | 6,945,000 | 7,755,000 |
| Japan (Yokohama) | 3,122,000 | 3,430,000 |
| India (Calcutta) | 275,000 | 350,000 |
| Total exports from Asia | 10,475,000 | 11,775,000 |

(Lyons Silk Merchants' Union.)

The importations of raw silk into the United States for the last five years have been as follows:

| | | |
|---|---|---|
| 1895 | 7,974,810 pounds, | valued at $22,029,068 |
| 1896 | 8,000,621 " | " " 26,246,902 |
| 1897 | 6,518,612 " | " " 18,496,944 |
| 1898 | 10,815,162 " | " " 31,446,800 |
| 1899 | 9,691,145 " | " " 31 827,061 |

# CHAPTER X.

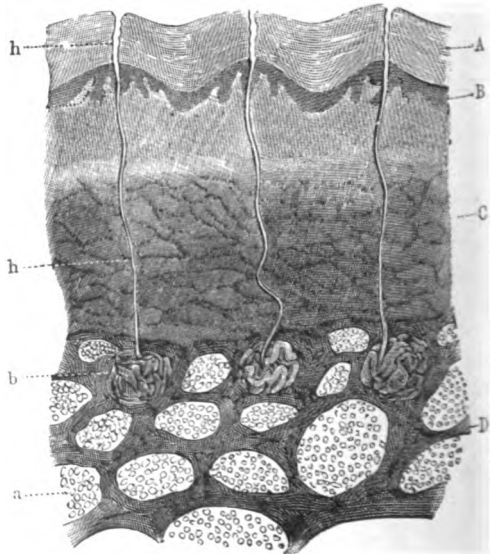
## ANIMAL TISSUES AND THEIR PRODUCTS.

### *A*. LEATHER INDUSTRY.

### I. Raw Materials.

1. ANIMAL HIDES AND SKINS.—The moist animal skin undergoes decomposition very rapidly; if dried becomes stiff and horny, or if boiled with water is changed into soluble glue. The object of tanning is to bring the animal skin into such a condition that decomposition is arrested, and after drying it no longer forms a stiff horny mass, but an opaque tissue insoluble in water, distinctly fibrous and pliable. The product known as leather has properties which at once distinguish it from the untanned hide, such as greater or less impermeability to water and toughness and strength. Nevertheless, the best authorities on the subject believe that in the main tanning is a physical rather than a chemical process, and that the function of the tanning material is chiefly to penetrate the pores of the skin and envelop the individual fibres so that in drying they are prevented from adhering and so stiffening the whole mass. The power of the skins to fix tanning materials upon the surface of its fibres varies considerably according to the nature of the material used, and in many grades of leather is undoubtedly supplemented by a chemical combination of the coriin of the skin with the tannin.

FIG. 96.

To understand the nature of the change wrought by tanning in the animal hide, it is necessary first to refer briefly to its anatomical structure. Fig. 96 shows a section of ox-hide cut parallel with the hair, magnified about fifty diameters. It consists essentially of three layers: the *epidermis*, which is itself made up of two layers, the outer horny layer or cuticle *A*, a dead layer which is continually wearing off and being renewed, and the inner mucous layer *B*, the *rete Malpighi*, a watery cellular layer, which rests upon the true skin and is continually renewing the outer layer; the *derma* or *corium*, the true skin, *C*, which alone is the leather-making tissue; and the *fatty under tissue*, shown in the illustration at *D*, in

which the perspiratory and sebaceous glands are embedded. Both the epidermis and the under tissue are removed in the preparatory processes of tanning, so that the corium alone remains to combine with the tanning materials to form leather. The hair of the animal is enclosed in hair-sheaths, which pass down through the epidermis and rest upon the corium, from which in life the hair-glands draw their nourishment. The corium, or true leather-forming layer, is composed of bundles of interlacing fibres, between which is found an albuminoid substance, *coriin*, which as the skin dries cements the fibres together and stiffens the hide. This is insoluble in water but soluble in lime-water, and hence removed in large part by the process of liming to which the hides are submitted.

The animal skins which are utilized in the manufacture of leather are, first, those of the ox, cow, buffalo, horse, etc. These are known as *hides*, or if from younger animals of the same kind as *kips*. Second, those of the calf, sheep, goat, deer, etc. These are known as *skins*. For special purposes the skins of crocodiles, alligators, porpoises, and seals are also made into leather.

The hides may come to the tannery according to the source whence obtained either as *fresh* or *green* hides,—that is, direct from the slaughter-houses,—as *wet salted*, as *dry salted*, and as *dried* hides. In addition to the domestic production, great numbers of hides are imported into the United States from the Argentine Republic and the River Plate in South America. England imports from India, the Cape of Good Hope, and Australia as well as from South America. Goat-skins for the morocco trade are brought mainly from India and the East.

2. Tannin-containing Materials.—The conversion of the hides into leather is usually accomplished by the action of an extract or infusion of tannin or tannic acid. This powerful astringent acid is very widely distributed in nature, being found in barks, roots, leaves, seed-pods, flowers, and fruits, and in excrescences on trees. More accurately speaking, we find a number of varieties of tannic acid in these different vegetable sources, of which some are more valuable for tanning than others. As a class they are readily soluble in water, amorphous, of slight acid reaction, and astringent taste. They yield with iron salts bluish-black or greenish precipitates, throw gelatine and albumen out of solution, and change hides into leather. In tanning it is not necessary to extract the acid in a pure state, but infusions are made from the powdered barks as needed, or concentrated extracts prepared for this purpose are used. We will note briefly the more important tannin-containing materials used at the present time in leather manufactures.

*Oak-bark.*—The common English oak (*Quercus Robur*), which includes the two varieties *Q. pedunculata* and *Q. sessiliflora*, is one of the most important materials. It contains from twelve to fifteen per cent. of tannic acid and produces an excellent quality of leather. Other varieties in use are *Quercus coccifera* (or kermes-oak), of which the bark, known as *coppice-oak*, is yellowish-brown in hue and very rich in tannin; *Quercus suber* (or cork-oak) and *Quercus Ilex* (or evergreen-oak), both of which are grown in Algiers, Italy, Spain, and the South of France. In the United States the most important varieties of oak are *Quercus prinus* or *castanea* (chestnut-oak); *Quercus rubra* (common red-oak); *Quercus alba* (or white-oak). The tannin of the several varieties of oak is known as *quercitannic acid.*

According to the researches of Etti,* the main constituents of the oak-bark are *quercitannic acid* with the formula $C_{17}H_{16}O_9$; its first anhydride, *phlobaphene*, $C_{34}H_{30}O_{17}$; its second anhydride, $C_{34}H_{28}O_{16}$; its third anhydride, *Oser's oak-red*, $C_{34}H_{26}O_{15}$; and its fourth anhydride, *Löwe's oak-red*, $C_{34}H_{24}O_{14}$. Of these, the quercitannic acid and the phlobaphene are specially concerned in the tanning process.

*Hemlock-bark.*—The bark of the hemlock (*Abies Canadensis*) of Canada and the United States contains nearly fourteen per cent. of tannin. This is extensively used, either jointly with oak-bark (union tanned leather) or as a substitute for it, in the manufacture of sole-leather. It is said to produce a harder leather than oak-bark, but less pliable and more pervious to water. A solid extract from the hemlock-bark containing from twenty-five to thirty-five per cent. of a deep red tannin is prepared in large quantities for export. The production of this solid extract is said to be at present considerably over ten thousand tons per annum. Liquid extracts with fifty per cent. of solid matter are also largely sold.

*Pine-bark* is much used in Austria, Bavaria, and Southern Germany. It contains from seven to ten per cent. of tannin and considerable resinous extractive matter. It does not yield so good a leather as oak-bark.

Closely related and somewhat used are the barks of the *White Spruce*, the *Larch*, and the *Fir*.

*Willow-bark.*—Several species of the willow, notably *Salix arenaria* and *S. capræa*, are used in Russia and Denmark for the tanning of lighter skins, for the manufacture of glove leather and the so-called Russia leather. It is stated that the yearly consumption of willow-bark in Russia at present is some six and a half million kilos. against two and a half million kilos. of all other tanning barks. The percentage of tannin in the willow is usually given at from three to five per cent., although Eitner † found over twelve per cent. in several species.

*Chestnut-wood.*—The wood of the chestnut (*Castanea vesca*) contains from eight to ten per cent. of a tannin which closely resembles gallotannic acid. The extract, containing from fourteen to twenty per cent. of tannin, is used largely to modify the color produced by hemlock extract and for tanning and dyeing.

*Horsechestnut-bark.*—The bark of the horsechestnut (*Æsculus hippocastanum*) is also said to be used for the manufacture of an extract under the simple name of "chestnut extract," but such manufacture in the United States is very doubtful.

*Catechu* (or *Cutch*) is the name given the dried extract from *Acacia Catechu*, cultivated in India and Burmah, and containing forty-five to fifty-five per cent. of a special variety of tannic acid (catechu or mimotannic). The extract is evaporated until a semi-solid dark-brown product is obtained. This is exported in mats, bags, and boxes to European and American markets.

*Gambier or Gambir* (*Pale Catechu*) is the dried extract from the leaves of *Uncaria Gambier* and *U. acida*. It contains thirty-six to forty per cent. of a brown tannin which rapidly penetrates leather and tends to swell it, but taken alone produces a soft, porous tannage; it is largely used in conjunction with other materials for tanning both light and heavy leathers. It is exported from Singapore in pressed blocks and cubes. The catechutannic acid of cutch

* Wagner's Chemical Technology, 13th ed., p. 1051.
† V. Höhnel, Die Gerberinde, p. 90.

and gambier differs from gallotannic acid in giving a grayish-green precipitate with ferric salt and no reaction with ferrous salts; by giving a dense precipitate with cupric sulphate and none with tartar emetic. They also contain *catechin*, which is said to be an anhydride of catechutannic acid.

*Kino* is an extract somewhat resembling cutch, and is the dried juice from a variety of plants. Thus, the East Indian kino is obtained from *Pterocarpus marsupium*, the Bengal kino from *Butea frondosa*, the African from *Pterocarpus erinaceum*, and the Australian from the several species of *Eucalyptus*. It ordinarily forms small angular fragments of black lustrous appearance, brittle, and crumbling to brown-red powder. It contains thirty to forty per cent. of a tannin (kinotannic acid) analogous to catechutannic acid, together with phlobaphene.

*Sumach* consists of the powdered leaves, peduncles, and young branches of *Rhus coriaria*, *Rhus cotinus*, and other species of *Rhus*. Thus, Sicilian sumach, the most esteemed variety, is from *R. coriaria;* Spanish sumach is from several species of *Rhus*, and comes in three varieties, Malaga, Molina, Valladolid; Tyrolean sumach from *R. cotinus;* French from *Coriaria myrtifolia;* American from *R. glabra*, *R. Canadense*, and *R. copallina*. The leaves are collected while the shrub is in full foliage and cured by drying in the sun. They are then ground under millstones and the product baled. The sumach contains from sixteen to twenty-four per cent. of a tannin which seems to be identical with gallotannic acid. The American variety contains usually six to eight per cent. more than the European, but also contains more of a dark coloring matter, which renders it inferior to the Sicilian sumach for white leathers.

*Myrobalans* (or *Myrabolans*).—The fruit of several species of *Terminalia* found in Hindostan, Ceylon, Burmah, etc. Myrobalans varies in size from that of a small hazel-nut to that of the nutmeg. The tannin occurs in the pulp which surrounds the kernel. It is generally used in combination with other tanning materials to modify the objectionable color which some of the latter impart to the leather. By itself it produces a soft and porous tannage.

*Valonia* is the commercial name for the acorn cups of several species of oak, *Quercus ægilops* and *Quercus macrolepis*, coming from Asia Minor, Roumelia, and Greece. They are of a bright-drab color, and contain twenty-five to thirty-five per cent. of a tannin somewhat resembling that of oak-bark, but giving a browner color and heavier bloom. It is generally used in admixture with oak-bark, myrobalans, or mimosa-bark, because of itself it produces too brittle a leather.

*Mimosa-bark* (*Wattle*).—The bark of numerous species of *Acacia* (*A. decurrens* and *A. dealbata*) from Australia and Tasmania, contains from twenty-four to thirty per cent. of mimotannic acid. The bark comes into commerce chopped or ground and also in the form of an extract. It makes a red leather and is generally used in admixture.

*Divi-divi.*—The seed-pods of *Cæsalpinia Coriaria*, a small tree found in the neighborhood of Maracaibo, South America. The pods are about three inches long, brownish in color, and generally bent by drying into the shape of the letter S. It contains thirty to fifty per cent. of a peculiar tannin somewhat similar to that of valonia, but is liable to fermentation.

*Quebracho.*—This is the name applied to several South American trees possessing hard wood. They are *Aspidosperma Quebracho* (*Quebracho blanco*), *Loxopterygium Lorentzii* (*Quebracho colorado*). The wood and bark

of the latter contain from fifteen to twenty-three per cent. of a bright red tannin. Both the wood and the extract are used in tanning.

*Nutgalls* is the term applied to the excrescences on plants produced by the punctures of insects for the purpose of depositing their eggs. The principal commercial kinds are oak-galls (or Aleppo galls) and Chinese galls. The first of these are the product of the female of an insect called *Cynips*, which pierces the buds on the young branches of the *Quercus infectoria* and other species of oak. In the centre of the gall thus produced the larva is hatched and undergoes its transformation, boring its way out as a winged insect in five to six months. If the galls are gathered while the insect is in the larval state they are known as "blue" or "green" galls; if the insect has cut its way out they are known as "white" galls, and are of inferior character and less astringent. The best oak-galls contain from sixty to seventy per cent. of gallotannic acid.

The Chinese gallnuts are the product from the *Rhus semialata*, the leaves of which are punctured by an insect, the *Aphis Chinensis*. The nuts are of irregular shape but are very rich in tannin, containing about seventy per cent.

*Knoppern* are galls from immature acorns of several species of oak largely used for tanning in Austria. They contain from twenty-eight to thirty-five per cent. of tannin.

## II. Processes of Manufacture.

Leather may be manufactured from hides or skins by a number of methods, which may be summarized, however, under three heads,—viz., tanning by the use of tannin-containing barks or extracts; mineral tanning, using either chromium salts to make an insoluble leather, or alum and salt, as in "tawing;" and the manufacture of soft leather by treatment of the skins with oils.

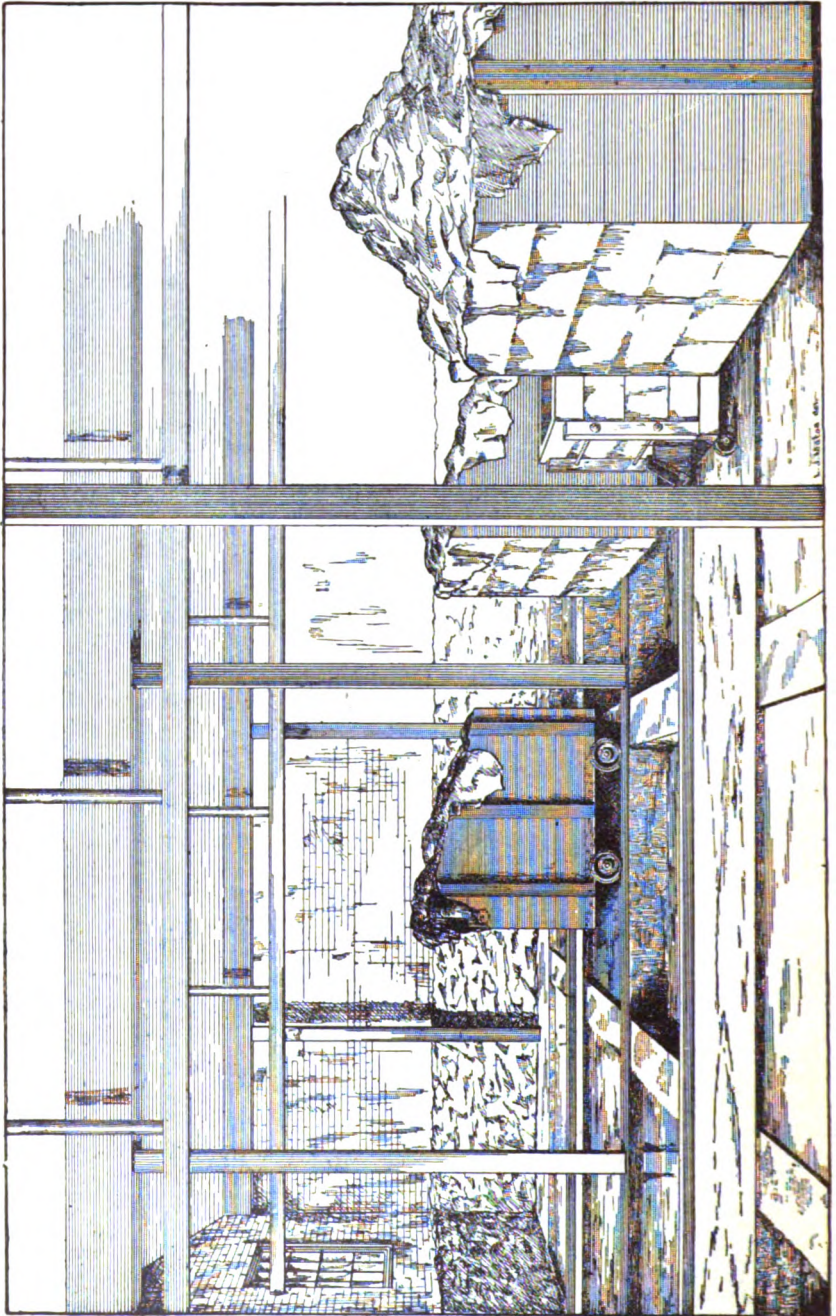
We will note first the methods involving the use of tannin-containing materials, and these again differ somewhat according to the grade of leather to be made and the character of the hides or skins used.

*A.* MANUFACTURE OF SOLE-LEATHER.—1. *Softening and Cleansing the Hides.*—This process differs according as the hides are taken in the fresh or green state or are salted or dried. For fresh hides, a washing with pure water to cleanse them from dirt and blood is all that is necessary to prepare them for the next or "swelling" process. For salted hides, a soaking in fresh water for from two to three days is necessary, while for hard dried hides a longer treatment is necessary, first in water which has been repeatedly used for softening and afterwards in fresh water. This involves often a slight putrefaction of the coagulated albumen of the dry hide. To control this and prevent injury to the corium of the hide a weak salt solution (five per cent.) is often used in this prolonged softening. "Stocking" or kneading the hides with heavy rolls or breaking weights is also needed for heavy hides which have been dried.

2. *Unhairing and Swelling.*—These operations are carried out together. As the swelling proceeds the cells in which the roots of the hair are embedded are softened, so that the hair is easily removed by mechanical means. The horny epidermis is similarly softened, so that it can be removed by the same means. The swelling may be effected by several different methods: (1) by *sweating*; (2) by *treatment with acid tan-liquor*; (3) by *liming*; (4) by *treatment with sulphides of sodium and calcium*, etc. The sweating process now

in use is the so-called "cold sweating" method, and consists in hanging the hides in a moist chamber kept at a uniform temperature of 60° to 70° F. (15° to 21° C.), so that an incipient putrefaction ensues which attacks the soft parts of the epidermis and root-sheaths before materially injuring the corium or leather-forming material. This method is that generally followed for sole-leather in this country and on the Continent of Europe, while in England liming is more generally adopted. The swelling with acid tan-liquor depends upon the action of the acids which are present in considerable quantity in old tan-liquors and their effect upon the connective tissue. The swelling and unhairing by lime always adopted for small skins is also used for sole-leather hides in England. A view of the lime-pits and skins in process of softening by lime as carried out in morocco tanneries is shown in Fig. 97. The action of the lime upon the hide is in part a solvent one. The hair-sheaths are loosened and dissolved and the hardened epidermis swells up and softens, so that both come away more or less completely with the hair when scraped. The intercellular substance, or coriin, as before stated, is also soluble in the lime-water, and as this is removed the fibrous nature of the leather-forming skin becomes more evident. The hides are generally put into several lime-pits in succession, in the first of which is old liquor with the weakest alkaline reaction because of its partial saturation with organic material, and in the last the liquor is the freshest and strongest in alkaline reaction. The hides require to be turned and changed in position during this liming process as well as removed from one pit to the other. The swelling and unhairing by the use of alkaline sulphides largely used upon the Continent of Europe consists in taking a solution of sodium sulphide (made from alkali-waste by Schaffner and Helbig's process) and bringing it to a thin pasty condition with lime. This is then spread upon the hair side of the hides and they are packed together for five to twenty hours, when the loosened hair and sulphide paste is washed off and the hides left in water a time longer to "plump" or swell. Another process uses the sulphide in solution only. The hair having been loosened by one or the other of the means just described, it is to be removed by mechanical means. This is usually done on the "beam," a sloping frame of wood or metal with a blunt two-handled knife, which pushes the hair downward and away from the workman. After the unhairing, the loose flesh and fat, the latter somewhat saponified by the lime, are next removed from the inner side of the hide by a sharp-edged knife. Hand "fleshing" is in many cases superseded by machine treatment, as the hide must not only be scraped but worked to force out the fat which remains in the loose tissue, as this would impede tanning. The hides after the fleshing are trimmed, and the inferior ends and edges are cut off with a sharp knife. They have still to be freed from the traces of lime which they have absorbed during the lime treatment before they can be put in the tan-liquors. This used to be done for sole-leathers, as it is still done for calf- and goat-skins, by means of "bate," or dung of animals, mixed with water, but that is now almost entirely replaced by the use of dilute acids which shall combine with the lime, when the lime salts so formed are to be washed out. Dilute sulphuric, phosphoric, and hydrochloric acids have been used (the latter being best because its lime salt is soluble), as well as the acid tan-liquors containing gallic, acetic, and lactic acids. The organic acids are considered to be safer for the hide than the inorganic.

3. *Tanning.*—The bark or other tanning material must be crushed and

FIG. 97.

then ground to a state sufficiently fine to allow of the extraction of the tannic acid, and yet not so fine as to cause it to cake together in clayey masses. This is accomplished in bark-mills and disintegrators of various kinds, which need not be specially described here. The tan-house into which the cleansed and prepared hides or "butts" now come is provided with rows of pits running in parallel lines, which are to contain the butts during their treatment with the tan-liquor. The butts in most cases are first suspended in weak tanning infusions before they go into the first, or "handler," pits. The object of this is to insure the uniform absorption of tannin by the skins before subjecting them to the rough usage of "handling," which in the early stages of the process is liable to cause injury to the delicate structure of the skin. During this suspension the skins should be in continuous agitation to cause the tannin to be taken up evenly. Both the suspension and the agitation are accomplished generally by mechanical means. From the suspenders the butts are transferred to the "handlers," where they are laid flat in the liquor. They are here treated with weak infusion of bark, commencing at about 15° to 20° by the barkometer (see p. 335), and are handled twice a day during the first two or three days. This may be done by taking them out, turning them over, and returning them to the same pit, or more generally by running them, fastened together, from one handler-pit into another. The treatment of the butts in the handlers generally occupies about six to eight weeks, by which time the coloring matter of the bark and the tannin should have "struck" through about one-third of the substance of the skin. Many of the butts will have become covered, moreover, with a peculiar "bloom" (ellagic acid) insoluble in water. They are now removed to the "layers," in which they receive the treatment of bark and "ooze," or tan-liquor, in progressive stages until the tanning is complete. Here the butts are stratified with ground oak-bark or valonia, which is spread between each butt to the depth of about one inch, and a thicker layer finally on top. The pit is then filled up with ooze, which varies in strength from about 35° barkometer at the beginning to 70° at the end of the treatment. For heavy tannages six to eight layers are required, the duration of each ranging from ten days at the beginning to a month in the later stages. Each time the butts are raised they should be mopped on the grain to remove dirt and loose bloom.

With the use of strong prepared extracts, especially with the aid of heat, the tanning process can be carried out in much shorter time than that just indicated, but the leather produced though hard is deficient in toughness and is liable to crack on bending sharply.

4. *Finishing.*—The butts after coming from the last layer are well brushed, washed in a clear liquor, and then thrown over a horse to drain before going to the drying-shed. They are then frequently oiled lightly on the grain so as to prevent too rapid drying out and hung on poles in the drying-loft. When about half dry, they are heaped upon the floor in piles and covered to sweat a little, which facilitates the operation of "striking," which next follows.

The "striking," which may be done by hand with a two-handled tool with triangular blunt edges or by machinery, is chiefly for the purpose of removing the deposit called bloom, although it somewhat flattens and stretches the leather. After a little further drying the butt is laid upon a flat bed of wood or metal and is rolled either by heavy hand-rollers or by the aid of machinery. The leather is then sometimes colored on the grain

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## OUTLINE OF TANNING PROCESS FOR SOLE-LEATHER.

Hides are taken either green, salted, or dried, and washed or soaked, as the case may be, with either water or weak brine to remove dirt and blood and to soften them, aided in the case of dried hides by "stocking," and useless ends trimmed off.

SOFTENED HIDES

unhaired generally either by sweating or by liming, and then worked on the beam.

UNHAIRED HIDES

are scraped or fleshed to remove flesh and fat, and then trimmed free from rough ends.

FLESHED AND TRIMMED HIDES

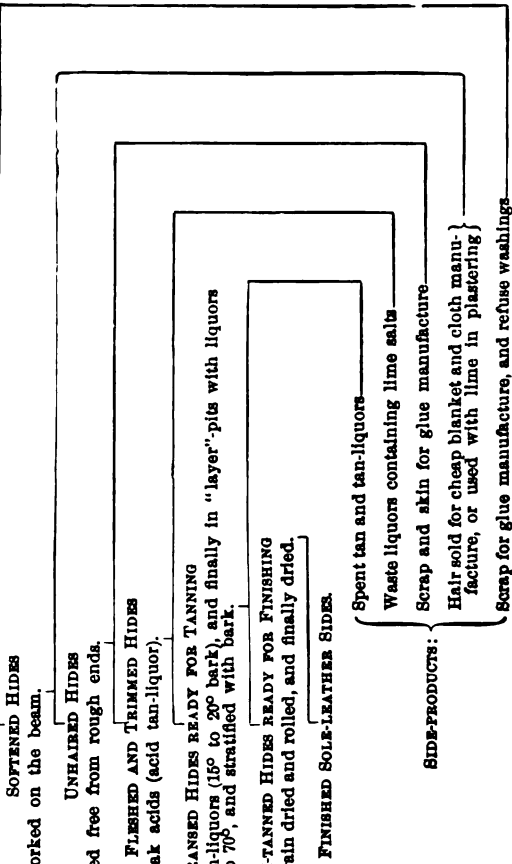
freed from lime by drench with "bate," or by washing with weak acids (acid tan-liquor).

CLEANSED HIDES READY FOR TANNING

are placed first in suspender-pits, then in "handlers" with weak tan-liquors (15° to 20° bark), and finally in "layer"-pits with liquors increasing in strength from 35° to 70°, and stratified with bark.

ROUGH-TANNED HIDES READY FOR FINISHING

are brushed, washed, and partially dried, sweated, and "struck." Again dried and rolled, and finally dried.

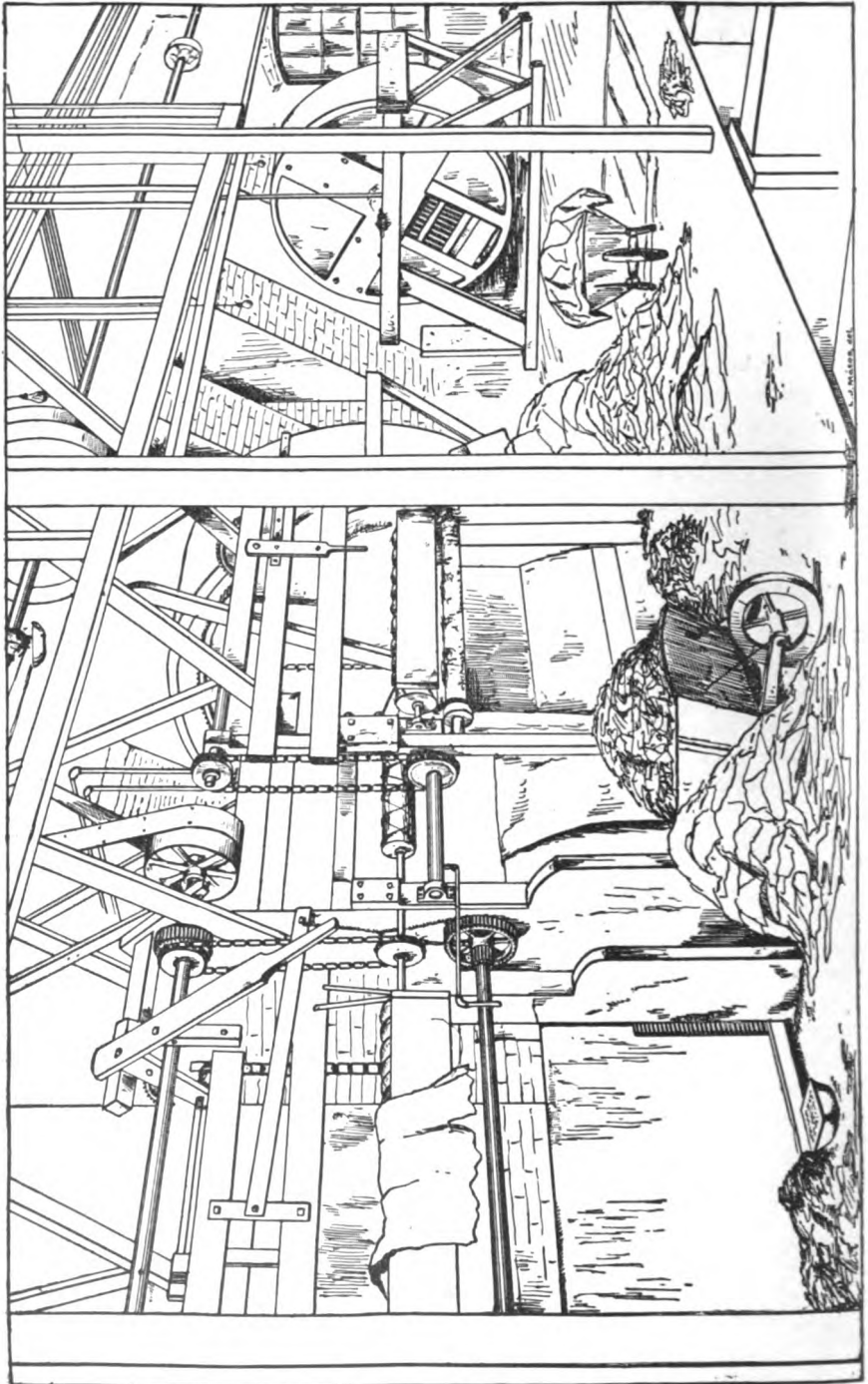
FINISHED SOLE-LEATHER SIDES.

SIDE-PRODUCTS:
- Spent tan and tan-liquors
- Waste liquors containing lime salts
- Scrap and skin for glue manufacture
- Hair sold for cheap blanket and cloth manufacture, or used with lime in plastering
- Scrap for glue manufacture, and refuse washings

with a mixture of yellow ochre, with size and oil to give a gloss, and then brushed again, well rolled, and dried off gradually in a room slightly warmed by steam. The main outlines of sole-leather tanning are summarized on the accompanying diagram.

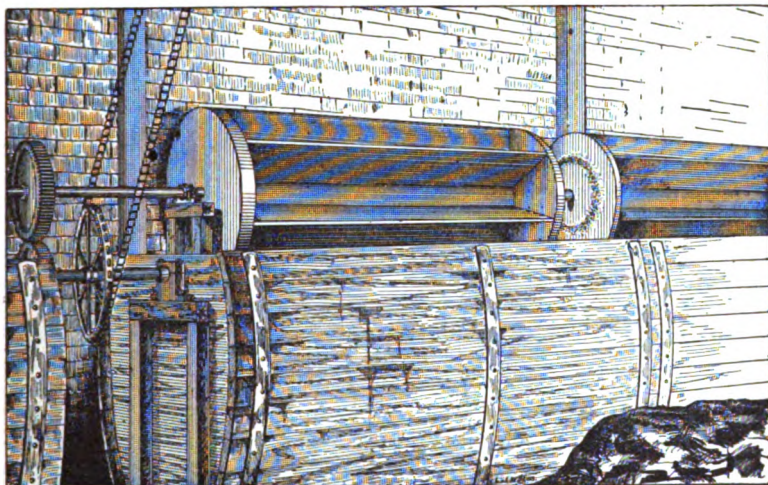
*B.* Upper and Harness Leathers.—For upper and harness leathers the hides of cows and smaller oxen are chosen. Fresh hides are, moreover, much better adapted for this class of leathers than dry salted or dry "flint" hides, as the utmost toughness and strength rather than hardness or weight are to be secured. The hides are cleansed, limed, and unhaired very much as already described for sole-leather. They are then "bated" in a bate of hen manure or treated with sour bran-liquor to completely remove the lime from the pores of the skin. The remaining portions of hair-sheaths and fat-glands are at the same time so loosened that they are easily worked out by a blunt knife on the beam. This final cleansing process is called "scudding." The action of the "bate" is considered by the best authorities to be a fermentative one, and the weak organic acids produced neutralize and remove the lime and at the same time soften the hide by dissolving out the coriin and probably also portions of the gelatinous fibre. "Stocking" is also used to assist in the softening and cleansing. These lighter tannages are also carried out very largely by the aid of gambier in combination with bark, valonia, mimosa, and myrobalans. The tanning liquors are often used at temperatures of from 110° to 140° F. (43° to 60° C.). The finishing of these light liquors requires much care in order to give them the proper softness and strength. They are alternately worked with a stretching-iron, or "sleeker," and rubbed with oil or with a mixture of dégras and tallow.

*C.* Morocco Leather.—This is generally made from goat-skins, although a cheaper variety is made from sheep-skins. The skins are softened and then unhaired by lime, to which a small quantity of arsenic sulphide is often added, whereby calcium sulphydrate and sulpharsenite are produced, which assist in softening the hair-sheaths and in giving the grain a higher gloss. A view of the unhairing machines and washing drums of a morocco tannery is given in Fig. 98. They are then bated with a mixture of dog's dung and water, known as the "pure." This is often followed by a treatment with bran to aid in removing the lime from the skins. A "scudding" or scraping with a blunt two-handled knife on both the grain and flesh sides then ensues to remove the last portions of lime salts and albuminoid matters. The tanning was formerly done with sumach and gambier, either in revolving paddle "tumblers," as shown in Fig. 99, or according to the English method, by sewing up the skins into bags partially filled with the sumach-liquor and then distended by air and floated in a large vessel of the same liquor. The bags are turned over constantly, and afterwards piled up in heaps. The sumach solution is thus forced through the pores of the skin, and the tanning is rapidly effected. The tanned skins are thoroughly washed and "struck," or scraped and rubbed, until smooth. After thorough drying they are again struck until thoroughly soft and smooth. This sumach tannage has been replaced in this country almost entirely by the chrome tanning, to be mentioned later.

*D.* Mineral Tanning or "Tawing."—Skins may be converted into a substance resembling leather, although in fact essentially different from it, by the action of alum and salt. There has been no chemical combination, however, analogous to that formed by the gelatine and tannic acid in the

Fig. 98.

ordinary tanning processes, as the gelatine, alum, and salt can be again separated by treatment with water.

The process of tawing is applied to goat, kid, sheep, and other small skins. The preliminary operations of steeping, breaking, liming, unhairing, and fleshing, steeping in bran-water and working on the beam, are essentially the same as have been described already. The skins with the pores cleared of lime and sufficiently opened are then put into a kind of wooden drum or "tumbler" such as are used for washing skins and for treating morocco leather skins with sumach solution. For every two hundred skins some twelve pounds of alum and two and a half pounds of salt with twelve gallons of water are used.

Fig. 99.

The action is continued for a short time only,—about five minutes. They are then put into an emulsion of yolk of eggs with flour and water, and tramped and worked in this until it has been thoroughly absorbed. The skins are now hung upon poles to dry, after which they are stretched and softened by drawing them to and fro upon the "stake," a blunt steel blade set in upright position.

"Combination tanning," in which the joint action of gambier and alum is used, is also extensively followed.

Very different from this kind of mineral tanning is that introduced within the last few years under the name of "chrome tanning." It depends upon the power of chromium oxide (sesquioxide of chromium) of forming an insoluble compound with the gelatigenous fibre of the hide, furnishing a product which possesses in a high degree the water-proof character desirable for leather.

The process generally in use at present in this country involves treating the skins at first with a weak solution of bichromate of potash to which sufficient hydrochloric acid is added to liberate the chromic acid (of course pickled skins may be used without the necessity of adding free acid). After the skins have taken up a bright yellow color through their entire texture they are drained and transferred to a bath of hyposulphite of soda to which some acid is added to liberate sulphurous acid, which reduces the

chromic acid to green chromic oxide. The sulphurous acid is at the same time oxidized to sulphuric acid, which liberates a further portion of sulphurous acid, until the whole of the chromic acid is reduced. Hydrogen sulphide liberated from alkaline sulphides has also been used as the reducing agent for bichromated skins, and still more recently electrolytic hydrogen developed upon the bichromated skin itself. In any case the reduction must take place rapidly, so that the potassium bichromate may be reduced superficially before it can "bleed" or diffuse out of the skins into the water of the reducing bath.

The leather so produced is of a pale bluish-green color, tough and flexible, and thoroughly resistant to water. Indeed, it is this latter property which distinguishes it from all other forms of leather, as the combination of the hide fibre or coriin with the chromium oxide is apparently more stable than its combination with tannin and yields less to boiling water, as has been shown in tests made by Professor Henry Procter, of Leeds. The leather can also be dyed and produced in a variety of colors, but the dyeing must be done before the leather dries, as its water-repellent character is such that once dried it cannot be wetted sufficiently to take up a full color.

Chrome-tanning processes involving the use of chrome alum and other salts of the sesquioxide of chromium as the basis of the tanning vat have been used, but apparently the combination does not take place so readily as where the chromium oxide is obtained in *statu nascendi* by reduction from the bichromate under the influence of reducing agents. Basic chromium salts, such as the basic chromium chloride, have also been proposed as mineral tanning agents, it being claimed that the dissolved chromium oxide is taken up by the hide-fibre at once and that a single bath only is necessary in this case. Such a basic salt is prepared by dissolving commercial chromium hydrate (chrome green) in hydrochloric acid, adding sal soda until precipitation of the hydrate begins again. The solution is then nearly neutral, and contains an oxychloride or basic chloride in solution. Common salt is also added to prevent injury to the grain of the leather and to facilitate tanning. After the absorption of the chromium oxide is completed the skins are agitated in water containing suspended carbonate of lime to neutralize all traces of acid. They are then washed and are ready for the fat liquor. At the present time the bulk of the glazed kid made in the United States is chrome-tanned, two establishments in Philadelphia each turning out at present three thousand dozen chrome-tanned goat-skins daily.

Quite recently formaldehyde, applied either as gas or in aqueous solution, has been introduced as a tanning agent, the well-known coagulating power of the formaldehyde on animal tissue causing it to unite with the hide fibre to form an insoluble leather. All grades of leather, from sole leather to light morocco, it is asserted, can be made readily and very rapidly by this treatment. As yet, it is too early to judge conclusively of its quality and durability.

*E.* Chamois and Oil-tanned Leather.—The skins tanned in this way are sheep- and calf-skins, and formerly chamois- and deer-skins. The flesh splints of sheep-skins are now generally employed for ordinary wash-leather. If heavy hides are taken, the grain side of the skin is shaved so that the oil can penetrate easily. The skins receive a thorough liming, so that the coriin is thoroughly removed from between the fibres, making them

very soft. A bran-drench follows to remove the lime, and they are worked on the beam. The surplus water having been removed by pressing, while still moist they are oiled with fish, seal, or whale oil (to which some five per cent. of carbolic acid is often added). After being stocked for two to three hours, shaken out, and hung up for one-half of an hour to an hour to partially dry, they are again oiled and stocked, and this process is repeated until the skins lose their original smell of limed hide and acquire a peculiar mustard-like odor. The later dryings are frequently conducted in a heated room, and when the oiling is complete the skins are piled up, and the oxidation of the oil which has already commenced during the fulling and drying is completed by a sort of a fermentation, in which the skins heat considerably. This heating must be controlled so that the leather is not injured, and if necessary the pile of skins is turned. When the oxidation is complete the skins are of the yellow chamois leather color. To remove the surplus oil, the skins are again oiled, then thrown into hot water and wrung out. The semi-solid fat obtained this way is the dégras so much prized for currying purposes. Or the whole of the uncombined oil is removed by washing with soda or potash lye and then set free by neutralizing with sulphuric acid. The oil so obtained forms the "sod oil" of commerce. About half of the oil employed is retained by the skin, and cannot be removed even by boiling with alkalies. No gelatine is obtained by boiling with water, to which the chamoised skin is much more resistant than ordinary leather. The skins intended for gloves, etc., are bleached like linen, by sprinkling and exposure to the sun or with weak solution of potassium permanganate followed by sulphurous acid.

## III. Products.

1. Sole-leather.—This is the heaviest and firmest variety of leather produced. It is made from the heaviest and thickest hides, and is valued for its fine grain and toughness. It retains the whole thickness of the hide, and no part is split off, so that it is not weakened by the loss of the flesh side. The tanning process is protracted until the whole hide is of uniform color throughout and shows the completed action of the tannin upon the interior of the hide.

2. Upper and Harness Leathers.—These are made from lighter hides, and are tanned for strength and flexibility rather than for weight, and are finished with care to give it perfect pliability. It may be shaved or split leather. The black color and finish are put on upper leather by coating it with a mixture of lamp-black, linseed oil, and fish oil, to which tallow and wax and a little soap have been added. This is brushed on, allowed to dry, and then thoroughly rubbed in and the skin sized with a glue size.

3. Morocco Leather.—The true morocco leathers are manufactured from goat-skins. A cheaper grade, known as French morocco, is produced from sheep-skins. As they are to be dyed on one side only, two of the skins are fixed face to face with the flesh side inward, so that the dye acts upon one side of each skin only. After dyeing the skins are rinsed and drained, saturated with linseed oil to prevent too rapid drying, and then curried by repeated oiling or waxing and rubbing with a glass "slicker."

4. Enamelled or Patent Leathers.—These are leathers finished with a water-proof and bright varnished surface similar to lacquered wood-

work. The name "enamelled" is generally applied when the leathers are finished with a roughened or grained surface, and "patent," or "japanned," when the finish is smooth. Thin and split hide are used. The skins after drying are prepared with a mixture of linseed oil and white lead and heated in closets to 160° F. (71° C.) or higher, then coated with a varnish of spirits of turpentine, linseed oil, thick copal varnish, and asphaltum, and heated again in closets or "stoves," as they are termed. This varnishing and heating are alternated, while the surface is meanwhile rubbed smooth with pumice, until the desired thickness is acquired.

5. RUSSIA LEATHER.—This variety is peculiar in its characteristic odor and ability to withstand dampness without any tendency to mould, both of which qualities it owes to the currying with the empyreumatic oil of birch-bark. In Russia the skins are tanned with willow-bark, but the imitation Russia leather made largely in Germany and England is tanned in the ordinary way with oak-bark. The birch-bark oil is rubbed into the flesh side of the tanned skins with cloths, care being taken not to apply so much as to cause it to pass through and stain the grain side of the leather. The red color is given by dyeing with Brazil-wood or red saunders, and the diamond-shaped marking by rolling with grooved rollers.

6. CHAMOIS LEATHER is a soft felt-like leather originally prepared from the skin of the chamois goat, but now made from other goat-skins and from the "flesh-splits" of sheep-skins. In these leathers the grain has practically been removed by scraping or "prizing" before the oil is applied, so that it is uniformly porous and soft throughout. They acquire a yellow color and a peculiar odor, although they are often bleached whiter by subsequent treatment. (See preceding page.) The combination of oil with the hide makes chamois leather very resistant to water and allows it to be washed without any change of nature.

7. WHITE-TANNED OR "TAWED" LEATHER.—Skins to be tanned with the hair on, as sheep-skin rugs, etc., are always alum-tawed, as well as light calf kid and glove leather. The glove leather obtained in this process has softness and considerable strength but is not thoroughly water-resistant, although the treatment with egg-yolk and flour-paste which follows the alum treatment tends to give them somewhat of this character.

8. CROWN LEATHER.—This is a variety which is intermediate between oil-tanned and tawed leather, being stronger than the first and more water-resistant than the latter. The hides are first tawed with the alum and salt mixture, then washed to partially dissolve out the tawing materials, and now spread upon a table and the flesh side covered with a mixture of fat, ox-brain, barley-flour, and milk. They are then put into a revolving tumbler and rotated for a time, and again rubbed with the fat mixture and rotated if necessary. The leather readily becomes mouldy, but seems to be strong and specially adapted for belting.

9. PARCHMENT AND VELLUM.—The first of these is prepared from the skins of sheep and goats and the second from the skins of calves. The skins are washed, limed, unhaired, and fleshed, again well washed, and then stretched either upon hoops or upon a square wooden frame called the *herse*. On these the skin while wet and soft is stretched thoroughly. It is then scraped again free from the fleshy matters, the flesh side dusted over with sifted chalk or slaked lime and rubbed in all directions with a flat piece of pumice-stone. The grain side is also scraped with a blunt tool and rubbed with pumice. The skin is then allowed to dry on the frame in the shade,

care being taken to avoid sunshine or frost. Very fine vellums are prepared with the finest pumice-stone.

10. DÉGRAS.—Among the side-products of the leather industry is one which is quite valuable for after-use. Dégras, originally obtained only as a side-product of the chamois-leather manufacture, is now also made specially on a large scale. The purest dégras is essentially an emulsion of oxidized fish oil produced by soluble albuminoids. That which is squeezed out of the skins after the completion of the fermentation and heating, which makes the last stage of the chamois-leather manufacture (see preceding page), is the finest grade of dégras. That which is recovered by the aid of caustic alkalies and after-liberation with sulphuric acid is the second grade (sod oil). The great demand for dégras for currying purposes has led to the manufacture of it as a special industry. The skins used for this purpose are treated exactly as in the normal chamois-leather manufacture, but are used over and over until no longer capable of taking up the oil. An artificial dégras has also been made from oleic acid, fat, and a little lime soap to which some tannic acid had been added.

Dégras is of semi-solid consistence and has a peculiar odor. Its specific gravity is higher than that of fish oil, and after dehydrating is from 0.945 to 0.955. Its characteristic constituent is the so-called dégras-former, which in a genuine dégras should range from twelve to twenty per cent. It is this which effects the ready emulsion with water. The dégras-former is a brown resinous saponifiable substance, fusing at from 65° C. to 67° C., and is distinguished from fats in that it is not precipitated when in alkaline solution by salt and is not soluble in petroleum-ether. According to Fahrion, the dégras-former is a mixture of oxy-fatty acids.

## IV. Analytical Tests and Methods.

1. QUALITATIVE TESTS FOR THE SEVERAL TANNING MATERIALS.—H. R. Procter * has constructed the following table (see p. 337) showing the reactions of the several tanning materials.

2. DETERMINATION OF STRENGTH OF TANNING INFUSIONS.—This is most rapidly and conveniently done in practice by the use of the specific gravity hydrometer. A special form of hydrometer constructed for tanner's use is known as a "barkometer." The zero point of the scale is taken by sinking the instrument in distilled water at 60° F., and the 10°, 20°, 30°, etc., marks gotten by plunging the instrument in ten, twenty, and thirty per cent. infusions of bark respectively. The intermediate degrees are then obtained by subdivision of the spaces as taken above. It is of course affected by the presence of other substances than tannin in the solution, and hence its indications are only comparable when taken on fresh or partially-used liquors, and not on old or spent liquors loaded with impurities.

3. QUANTITATIVE ESTIMATION OF TANNIN.—Of the numerous processes that have been described for this purpose, the only one generally accepted as capable of sufficient accuracy is Löwenthal's permanganate method. This depends upon the oxidation of the tannin, etc., by permanganate of potash in acid solution in the presence of indigo, which serves as indicator, as its oxidation shows the end of the reaction. As solutions of commercial tanning materials contain other oxidizable matters besides tannins,

* Text-book of Tanning, pp. 112 and 113.

it is necessary to separate these and titrate a second time in order to ascertain the volume of permanganate actually required by the tannin present. This separation may be effected by digestion with hide-raspings, or more conveniently by a solution of gelatine. In practice, a mixed solution of gelatine and common salt is used to which a small quantity of sulphuric or hydrochloric acid is added. Procter has also improved the process by adding kaolin, after the gelatine and salt have removed the tannin, for the purpose of facilitating filtration.

The special precautions and details of the process as generally practised and as modified by the Commission of German Technical Chemists are given in Allen.* The results are always stated in terms of crystallized oxalic acid to which the tannin is equivalent in reducing power upon the permanganate solution, and are gotten by the aid of the proportion $c:(a-b)::63:x$, in which $c$ represents the volume of permanganate needed for ten cubic centimetres of decinormal oxalic acid, $a$ and $b$ the volume of permanganate needed for the tanning infusion before and after precipitation of the tannin. Another method of a different kind is that of Simand and Weiss, as used in the Austrian Experimental Station for Leather Industry, which depends upon the absorption of tannin by hide-powder. An extract of the tannin-containing material of definite strength having been prepared,† an aliquot portion of the clear filtered solution is evaporated to dryness in a platinum dish until constant weight is obtained, ignited, and the weight of ash obtained and deducted. A second definite portion (some two hundred cubic centimetres) of the same solution is digested with hide-powder, using the rapid filtration apparatus devised by Procter,‡ and from the filtrate an aliquot portion evaporated as before, and the ash determined and deducted. The difference between the first and second weights of ash-free extract gives the tannin of the material used.

4. Determination of Acidity of Tan-liquors.—A method for the determination of volatile and non-volatile organic acids and the sulphuric acid present in acid tan-liquors has been given by Kohnstein and Simand.§ One hundred cubic centimetres of the tanning liquor is taken and eighty cubic centimetres distilled off, the residue diluted and again distilled with steam. The acidity of the distillate is determined, and the result is the *volatile organic acids* reckoned in terms of acetic acid. To determine the non-volatile organic acids, eighty cubic centimetres of the tanning infusion is treated with three to four grammes of freshly-ignited magnesium oxide and the mixture left for some hours with frequent agitation, when the filtered liquid will be nearly colorless and perfectly free from tannin. The magnesia in solution is determined in an aliquot part of the filtered solution, and will be equivalent to the *total free acids* of the liquor exclusive of the tannic acid. Another portion of the filtrate is evaporated to dryness, the residue gently ignited, moistened with carbonic acid water, and dried. It is then boiled with distilled water and the solution filtered. The carbonate of magnesia remaining insoluble represents the *total organic acids*, and can be more accurately determined by converting the magnesia into pyrophosphate and weighing. If these total organic acids be calculated in terms of acetic acid, and the previously found volatile acids, reckoned as acetic, be de-

* Allen, Commercial Organic Analysis, 2d ed., vol. iii. Part i. pp. 109–116.
† Horn, Chem. technische Analyse Organischer Stoffe, Wien, 1890, p. 236.
‡ Allen, Commercial Organic Analysis, 2d ed., vol. iii. Part i. p. 119.
§ Dingler, Polytech. Journ., 256, pp. 38 and 64.

| REAGENT. | Myrobalans. | Divi-divi. | Valonia. | Oak-bark. | Chestnut-wood. (Extract.) | Hungarian larch. (Extract.) | Hemlock. (Extract.) | Mimosa-bark. | Cutch. (Pegu.) | Gambier. (Cuba.) | Gallotannic acid one per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Boiled with equal volume of sulphuric acid (1:9 water). | Pale deposit on cooling (ellagic acid). | Pale deposit on cooling (ellagic acid). | Slight pale deposit. | Slight pale deposit or turbidity on cooling. | Slight red deposit on cooling. | Yellow flocculent deposit, separates quickly. | Abundant red flocculent deposit. | Heavy red deposit on cooling. | Light-red deposit on cooling. | Reddish deposit on cooling. | Usually some pale deposit. |
| Bromine-water. | No precipitate. | No precipitate. | No precipitate. | Pale precipitate. | No precipitate. | Yellow precipitate. | Yellow precipitate. | Yellow precipitate. | Yellow precipitate. | Yellow precipitate. | No precipitate. |
| Dilute ferric chloride. | Blue-black precipitate. | Dark-blue precipitate. | Blue-black precipitate. | Bluish-black precipitate. | Blue-black precipitate. | Dull-brown precipitate. | Dirty-green precipitate. | Full-brown precipitate. | Green-black precipitate. | Intense green color. | Blue-black precipitate. |
| Add ammonia. | Brown precipitate. | Dark-red precipitate. | Red-brown precipitate. | Red-brown precipitate. | Dull-red precipitate. | Dull-red precipitate. | Reddened precipitate. | Purple color. | Dark-red precipitate. | Reddened. | Reddened precipitate. |
| Solution of tartar emetic. | No precipitate. | Faint clouding. | No precipitate. | No precipitate. | Slight clouding. | No precipitate. | No precipitate. | White precipitate. | No precipitate. | No precipitate. | No precipitate. |
| Add ammonic chloride. | Light precipitate. | Dense precipitate. | Pale precipitate. | Whitish precipitate. | Pale precipitate. | Pale precipitate. | Slight pale precipitate. | Dense white precipitate. | Pale precipitate. | Faint clouding. | White precipitate. |
| Copper sulphate. | Faint clouding. | Slight green precipitate. | No precipitate. | Slight precipitate. | No precipitate. | Slight clouding. | Pale precipitate. | Slight precipitate. | Dense precipitate. | No precipitate. | No precipitate. |
| Add ammonia. | Dense dark precipitate. | Dense dark precipitate. | Dark-reddish precipitate. | Brown precipitate. | Dark-brown precipitate. | Deep-blue coloration. | Dark-green coloration. | Deep-red precipitate. | Deep violet coloration. | Dark-green color. | Brown precipitate. |
| Lime-water. | Yellow precipitate turning greenish. | Yellow precipitate turning purple. | Yellow precipitate turning red-purple. | Brown precipitate. | Purplish-brown precipitate. | Dirty-brown precipitate. | Brown precipitate. | Slight reddish precipitate. | Slight clouding, soluble in excess. | No precipitate. | Pale precipitate, turns blue. |
| Ammonic molybdate in nitric acid. | Dirty-yellow precipitate. | Dark-greenish precipitate. | Dark-greenish precipitate. | Greenish precipitate. | Dirty-green precipitate. | Slight clouding. | Slight precipitate. | Brown precipitate. | Slight clouding, soluble in excess. | No precipitate. | Yellow color. |
| With sodic sulphide exposed to air on a tile. | Yellow color. | Yellow color. | Turns purplish-red. | Turns red. | Reddish precipitate. | No change. | No change. | Turns red. | Slight reddening. | No change. | No change. |
| Add concentrated sulphuric acid to one drop of infusion. | Yellow color. | Intense crimson. | Deep yellow. | Deep-red precipitate on dilution. | Dark brown. | Dark-brown or crimson. | Intense crimson. | Intense purple-red. | Deep red, no precipitate on dilution. | Dark brown or crimson. | Yellow. |
| Lead nitrate. | Light-yellow precipitate. | Dark-yellow precipitate. | Pale precipitate. | Brown precipitate. | Brown precipitate. | Pale precipitate. | Pale precipitate. | Clouding. | No precipitate. | Faint clouding. | White precipitate. |
| Cobalt acetate. | Buff precipitate. | Buff-pink precipitate. | Dirty-pink precipitate. | Brown precipitate. | Dirty-yellow precipitate. | Purplish precipitate. | Purple precipitate. | Brown precipitate. | Brown precipitate. | No precipitate. | Purple precipitate. |
| Manganese acetate. | Yellow precipitate. | Yellow precipitate. | Dirty-yellow precipitate. | Brown precipitate. | Gray precipitate. | Slight clouding. | Slight precipitate. | No precipitate. | No precipitate. | No precipitate. | White precipitate. |
| Uranium acetate. | Dark-red color. | Dark-red color. | Dark-red color. | Dark-brown precipitate. | Dark-red color. | Slight darkening. | Light-brown precipitate. | Dark-red color. | Dark-red color. | Dark-red color. | Crimson color. |
| Ammoniacal picric acid solution. | No precipitate. | No precipitate. | Brown precipitate. | No precipitate. | No precipitate. | No precipitate. | Clouding. | No precipitate. | No precipitate. | No precipitate. | No precipitate. |
| Potassium dichromate. | Brown precipitate. | Brown precipitate. | Brown precipitate. | Brown precipitate. | Brown precipitate. | No precipitate. | Brown precipitate slowly formed. | Brown precipitate. | Brown color. | Brown precipitate slowly formed. | Brown precipitate. |

ducted, the difference represents the *non-volatile organic acids*. The magnesia remaining in the filtrate from the carbonate of magnesia is combined as sulphate, and when determined gives the *sulphuric acid* of the original liquors.

5. ANALYSIS OF LEATHER.—It is possible in the case of a leather to determine the percentage of moisture, total fats, water-soluble matter, insoluble fibre, and ash. In the case of mineral tannages, the quantitative determination of the chief constituents of the ash is of special importance. The fats are determined by extraction in a Soxhlet apparatus, as described in a previous chapter, carbon disulphide or petroleum-ether being used as solvent. The dry leather residue remaining after this extraction is digested for some hours with distilled water at 40° C. and then thoroughly extracted by fresh water at the same temperature. The washings are then brought to fixed volume and the residue determined in an aliquot portion. Uncombined tannin may also be determined in this aqueous extract by means of the hide-powder or Löwenthal method. The total ash is obtained by igniting a separate quantity of the leather. This is chipped in small fragments and ignited gradually in small portions in a platinum dish. After the leather swells and carbonizes, it can be burned completely at a dull-red heat without loss of the mineral salts.

## *B.* GLUE AND GELATINE MANUFACTURE.

Glue is a decomposition product of many nitrogenous animal tissues. These lose on heating with water (analogous to starch-granules) their organized structure, swell up, and gradually go into solution. The solutions, even when very dilute, gelatinize on cooling, forming a jelly, which dries to a horny translucent mass. This mass is glue or gelatine, as the finer grades are termed. It dissolves in hot water to a liquid possessing notable cementing power. Neither the original solution obtained from the nitrogenous tissues nor the jelly formed from it on cooling have any cementing power. This is only acquired when the jelly has dried to the hard mass known as the glue. Two proximate principles seem to be present as characteristic in all preparations of glue: *glutin*, obtained chiefly from the hide and larger bones, and *chondrin*, from the young bones while yet in the soft state and the cartilage of the ribs, and joints. Of these, the former much exceeds the latter in adhesive power, and is therefore sought to be obtained predominantly in the glue manufacture.

### I. Raw Materials.

1. HIDES AND LEATHER.—The corium of the animal hides (see p. 305) is the most important glue-yielding material to be had. Neither the epidermis nor the underlying fat-tissue contribute to the glue production, but have rather an injurious effect when present. What is known as "gluestock" is made up of the trimmings from the ox, sheep, and calf-skins, the refuse of the beam-house, and scraps of parchment which have been softened and unhaired by liming and are in condition for immediate boiling. Of still greater value are the so-called calves' heads, which after liming and drying form a special article of commerce. The amount of glue obtainable from these various materials varies from fifteen to sixty per cent. According to Fleck,* the scraps from the alum-tawing process yield forty-five per

* Die Fabrikation Chemischer Producte, etc., p. 60.

cent., those from the ox-hides thirty per cent., hare- and rabbit-skins and parchment trimmings fifty to sixty per cent., foot and tail pieces of oxen fifteen to eighteen per cent., other scraps from the tanneries, such as ear-laps of sheep and cows, sheep's feet, etc., thirty-eight to forty-two per cent. Scraps of bark-tanned leather, such as shoemaker's and saddler's trimmings, are also available after a special treatment for the removal of the tannin. (See p. 341.)

2. BONES.—The bones contain on an average nearly one-third (32.2 per cent.) of their weight of organic constituents, extracted by boiling and converted into glue, which, however, is inferior in adhesive power to that prepared from animal skins. The soft bones of the head, shoulders, ribs, legs, and breast, and especially deer's horns and the bony core of the horns of horned cattle, yield a larger quantity of glue than the hard thigh-bones and the thick parts of the vertebra, which are principally composed of calcium phosphate and require a more prolonged treatment to extract the glue-making constituents.

3. FISH-BLADDER.—The inner skin of the air-bladders of the several varieties of sturgeon and cod furnishes a very pure glue substance, which on account of its purity is preferably used for culinary and medicinal purposes, and is known as "isinglass." It is inferior in adhesive power to hide-glue, but on account of its freedom from color, taste, and odor, and its almost perfect solubility in hot water, commands a higher price. It is used for food preparations, for clarifying wine, beer, and other liquids. The chief production of isinglass is from the sturgeon in Russia, on the borders of the Caspian and the Black Sea.

4. VEGETABLE GLUE.—Certain species of algæ (*Plocaria tenax* and others) found in Chinese and Japanese waters when cleansed and boiled yield a product known under the several names of "Chinese isinglass" and "agar-agar." Of similar character is no doubt the "algin" recently obtained from Scotch algæ by E. C. C. Stanford.*

## II. Processes of Manufacture.

1. MANUFACTURE OF GLUE FROM HIDES.—The hide trimmings and offal, if in the fresh state, must first of all be well limed,—that is, treated with milk of lime in pits for a period varying from ten to forty days, according to the character and source of the hides, the lime being frequently renewed. The lime softens and swells the hide-tissue, saponifies the fats, and dissolves in large part the coriin, blood, and flesh-particles which do not form glue. The glue-stock is then thoroughly washed free from the lime, lime salts, and dirt, usually by putting it in nets or wicker baskets which are suspended in running water. The liming also serves to preserve the glue-stock in case it is not to be immediately worked up. After washing it is spread out to dry. The lime scum from the pits is often utilized in fertilizer manufacture. Caustic soda has also been used instead of milk of lime for this treatment. A short treatment with chloride of lime immediately after taking the stock out of the lime-pits has also been found to give the glue a bright color and excellent adhesive power. In recent years sulphurous acid has been used with advantage to cleanse and prepare the glue-stock, as it bleaches and at the same time swells the hide, at least as well as can be done by the lime.

* Soc. Chem. Ind. Jour., 1884, p. 297.

The boiling and conversion of the glue-stock into solution may be effected by heating with water or with steam. The older method was to place the glue-stock in large kettles, but supported upon a false bottom of perforated metal, and adding water to heat it by direct fire. When the whole quantity of water necessary to convert the hides, etc., into glue solution is used at once, the drawback is encountered that the gluten which first goes into solution becomes altered by the prolonged heating and loses its adhesive power. This can be obviated somewhat by using successive smaller portions of water and drawing them off as they become saturated, but the last portions extracted are then darkened in color. The use of steam, either from closed pipes or direct steam from perforated pipes, greatly improves the extraction, shortening the time required and improving the quality of the product. A form of boiler for this glue manufactured by the aid of steam as devised by Dr. B. Terne is given in Fig. 100. Direct high-pressure steam blown into closed vessels has been found to be quite effective in rapidly melting down the glue-stock and producing a concentrated solution.

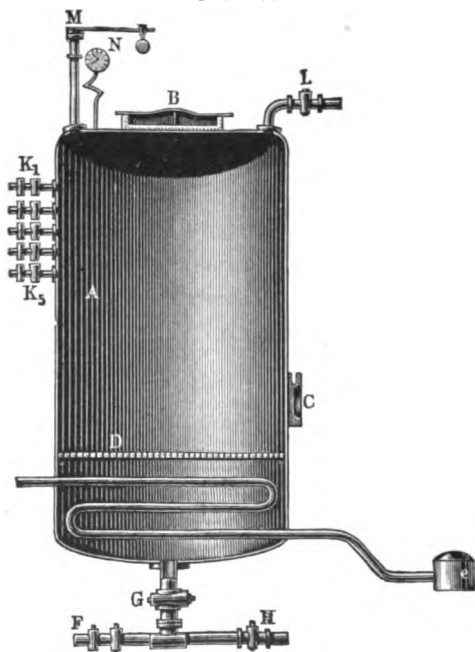



FIG. 100.

The use of vacuum-pans and the extraction by steam under reduced pressure and at lower temperatures has also been found very satisfactory in giving a good product in which the adhesive qualities of the gluten are in no way impaired. The solution must be freed from any melted fat and lime soaps by skimming and from suspended impurities by settling, by filtering through linen bags, or clarifying by the use of bone-black. The addition of alum as sometimes practised has an injurious effect upon the adhesive power of the product. The residue of the glue-stock left unextracted is pressed out, dried, and sold as a fertilizer containing about four per cent. of nitrogen. The clarified glue solution is poured into shallow wooden moulds some six inches in depth, in which as it cools it gelatinizes to a brownish-yellow jelly containing from eighty to ninety per cent. of water. The block of jelly is then turned out upon a smooth table, previously moistened to prevent adherence, and sawed by horizontal wires into thin slabs, which are again cut by vertical wires into strips of the proper width.

The drying of the jelly is one of the most troublesome parts of the whole process, as it must take place rapidly so that the glue-making material may not spoil, as it is very prone to do while in the jelly form, and, on the other hand, the heat should not exceed 20° C. (68° F.). It may take place with this limitation of temperature in the open air, if the air is not

too moist or too dry, both of which conditions are unfavorable. It is now generally effected in drying-rooms in which a current of warm dry air at the right temperature is made to circulate. As the surface of the cakes after drying is generally rough and dull, it is improved in appearance by moistening with warm water, brushing with a soft brush, and again drying.

2. MANUFACTURE OF GLUE FROM LEATHER-WASTE.—Before attempting to boil the leather-waste to glue, the removal of all traces of tannic acid becomes absolutely necessary, since the retention of the smallest quantity prevents the animal tissue from dissolving in water. The waste must therefore be comminuted as thoroughly as possible to facilitate the complete removal of the tannic acid. This is done frequently in the "hollander" used for paper-pulp, and the washed and ground leather-waste then heated in a pressure-boiler under a pressure of two atmospheres with fifteen per cent. of its weight of slaked lime. After thorough washing the residue is ready for use as glue-stock.

3. MANUFACTURE OF GLUE OR GELATINE FROM BONES.—Two methods have been followed for the extraction of gelatine, as the product is generally called in this case, from bones. The bones are either boiled under pressure, or they are treated with hydrochloric acid to remove the calcium phosphate and afterwards boiled for the extraction of the gelatine. The bones in either case are with advantage deprived of their fat first, which is done either by heating them with water and steam in boiler-shaped vessels, when the fat rises and can be skimmed off from the water, or in closed vessels with volatile solvents like petroleum-benzine and carbon disulphide. The older process of extracting the gelatine by boiling the powdered bones with water under pressure decomposes a portion of the valuable material, and is now generally replaced by the method of treatment with hydrochloric acid for the removal of the calcium phosphate. The crushed bones are placed in wooden vats with dilute hydrochloric acid of specific gravity 1.05 (forty litres of acid to ten kilos. of bones) and allowed to remain for several days. They are then placed in lime-water for a time, well washed, and boiled eight to ten hours with a large excess of water, or converted more rapidly into gelatine solution by the aid of steam. The resulting solution is filtered through cloth, bleached by sulphurous oxide, and poured into forms to gelatinize. The manufacture of bone gelatine is frequently combined with the fertilizer manufacture, as the calcium phosphate extracted by the hydrochloric acid treatment contains from eighteen to twenty per cent. of phosphoric acid. The newer method of extracting the fat by volatile solvents yields five to six per cent. of fat without injury to the gelatine of the bones, while the older method of boiling out the fat yields from three to four per cent. only and tends to lessen the yield of gelatine.

4. MANUFACTURE OF FISH GELATINE.—The swimming-bladders of the fish are taken and thoroughly washed in water from all fatty and bloody particles. They are then removed and cut longitudinally into sheets, which are exposed to the sun and air to dry, with the outer face turned down, upon the boards of linden or bass-wood. The inner face of the bladders is pure isinglass, which when partially dried can with care be removed from the outer muscular layer. The isinglass layer, possessing a silvery white lustre, is taken either in sheets, rings, or horseshoe-shaped strips, etc., bleached with sulphurous acid, and then thoroughly dried.

A product distinct from isinglass and known as fish glue is prepared by boiling the skin and muscular tissue of fish, and more resembles ordinary hide glue in its adhesive properties, but is offensive in odor. It is prepared from the scales and skins of large fish like the carp by acting on them with hydrochloric acid as upon bones and then extracting with water.

## III. Products.

1. Hide Glue is the variety which shows most strongly the adhesive property, and hence is that manufactured for joiner's and carpenter's use. Its color may vary considerably without any impairing of its adhesive power. It is rarely perfectly colorless or transparent. A gray to amber or brown-yellow color and translucent or partially opaque appearance is more usual. It should be clear, dry, and hard, and possess a glassy fracture. It should swell up but not dissolve in cold water, but dissolve in water at 62.5° C. (144.5° F.). Inorganic substances (such as white lead) are intentionally introduced into some varieties, such as the Russian glue, without injury to their adhesive power.

The variety known as "Cologne glue" is manufactured from scrap hide, which after liming is carefully bleached in a chloride of lime bath and then thoroughly washed.

"Russian glue," as stated, contains some inorganic admixture. It is of a dirty-white color, and contains from four to eight per cent. of white lead, chalk, zinc-white, or barytes.

"Size glue" and "Parchment glue" are both skin glues prepared with special care.

2. Bone Glue (or Bone Gelatine).—Bones yield a product of less adhesive power than the glue of skins and tendons, but when carefully worked the product is clearer and is free from offensive odor. It is therefore much used for culinary purposes and for medicinal applications, and for fining or clarifying beer, wine, and other liquids it has largely superseded isinglass. The gelatine thus used must, however, be absolutely tasteless and free from odor.

Bone gelatine is now made use of very largely in the manufacture of gelatine capsules, etc., for medicinal uses, of court-plaster for applying to wounds, and of gelatine emulsions with bromide and chloride of silver for coating the photographic dry plates. Mixed with glycerine it makes an elastic mass used for printer's rolls, for hectographs, etc.

"Patent Glue" is a very pure variety of bone glue of deep dark-brown color. It is very glossy and swells up very much in water.

3. Isinglass (or Fish Gelatine).—This is the finest and best of animal glues. The best isinglass should be pure white, nearly transparent, dry and horny in texture, and free from smell. It dissolves in water at from 35° to 50° C. (95° to 122° F.) without any residue, and in cooling should produce an almost colorless jelly. The commercial varieties of isinglass are the *Russian* (the best coming from Astrachan), *North American* (or *New York*), *East Indian*, *Hudson's Bay*, *Brazilian*, and *German* (or *Hamburg*).

4. Liquid Glue.—By the action of nitric or acetic acid upon a solution of glue its power to gelatinize may be completely arrested while its adhesive power is not at all interfered with. Thus, if one kilo. of glue is dissolved in one litre of water and .2 kilo. of nitric acid of 36° B. be added, after the escape of the nitrous fumes we have a solution that will not gela-

tinize on cooling, although it has the full adhesive power of the glue. Four parts of transparent gelatine, four parts of strong vinegar, one part of alcohol, and a small amount of alum will also yield an excellent liquid glue.

## IV. Analytical Tests and Methods.

The nature of glue makes it rather a question of physical and mechanical tests as to quality of a given sample than of chemical tests.

1. ABSORPTION OF WATER.—Thus the relative amount of water that a given sample will take up when laid in cold water is regarded as a moderately fair criterion of its quality. A weighed sample is laid for twenty-four hours in cold water (not exceeding 12° C. (53.4° F.) in temperature), and at the expiration of that time the excess of water having been poured off, the jelly is weighed. Very good varieties (white gelatine prepared from bones) will take up thirteen times the quantity of water in gelatinizing, second quality glue ten times, and inferior grades only about six times the amount of water. At the same time the *consistency* of the jelly formed must also be taken into consideration. A firm jelly produced by the absorption of a large quantity of water indicates a glue of the best quality.

Two observations are of value in this connection: first, glue twice dissolved and again dried is capable of drying out more thoroughly and of showing water-assimilating properties on redissolving more fully than glue obtained by a single drying; and, second, that hide glue on taking up smaller quantities of water becomes very soft and more difficult to weigh accurately than bone glue, which, with larger amounts of absorbed water, still forms a firm jelly. This difference in behavior alone is capable of giving an indication of the source of the glue.

2. INORGANIC IMPURITIES.—The presence of inorganic salts, as in the case of Russian glue, can be determined by the use of the appropriate reagents, and the amount also quantitatively determined.

3. ADULTERATION OF ISINGLASS WITH GLUE.—Isinglass is sometimes adulterated by rolling up sheets of gelatine (bone gelatine) between the layers of true isinglass and drying them in this condition.

Redwood and Letheby have observed that the ash of pure isinglass does not exceed .9 per cent., while glue contains from two to four per cent. of ash. An adulterated sample of isinglass gave Letheby 1.5 per cent. of ash.

On heating with water, true isinglass gives only a peculiar fish or algæ odor, while the adulterated isinglass gave a strong glue-like odor at once recognizable.

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## STATISTICS.

1. Importations of Tanning Materials into the United States.—

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Gambier, or terra Japonica, pounds | 29,022,203 | 32,338,264 | 31,349,545 | 42,334,590 | 38,123,478 |
| Valued at | $963,255 | $1,108,611 | $959,501 | $1,021,341 | $754,497 |
| Sumac (ground), pounds | 12,179,203 | 13,432,041 | 18,688,635 | 8,301,235 | 12,975,970 |
| Valued at | $235,157 | $232,570 | $248,048 | $120,205 | $183,136 |

2. Importations of Tanning Materials into Great Britain.—

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Cutch and gambier, tons | 25,545 | 26,844 | 25,048 | 19,504 | 21,526 |
| Valued at | £556,120 | £549,256 | £418,128 | £304,808 | £347,025 |
| Valonia, tons | 35,605 | 31,605 | 29,637 | 25,882 | 24,336 |
| Valued at | £395,943 | £319,798 | £300,324 | £270,802 | £281,471 |

3. Importations of Tanning Materials into Germany.—

| | 1893. Metric tons. | 1894. Metric tons. | 1897. Metric tons. | 1898. Metric tons. | 1899. Metric tons. |
|---|---|---|---|---|---|
| Catechu | 5,719 | 5,969 | 5,791 | 6,487 | 7,237 |
| Divi-divi | 6,633 | 4,874 | 9,315 | 7,140 | 8,522 |
| Gallnuts | 2,418 | 3,059 | 2,462 | 2,869 | 2,497 |
| Myrobalans | 5,070 | 7,911 | 10,230 | 10,884 | 9,945 |
| Quebracho-wood | 39,016 | 40,175 | 81,497 | 113,506 | 80,298 |
| Tanning extracts | 9,246 | 11,313 | 17,472 | 22,934 | 28,959 |

4. UNITED STATES IMPORTATIONS OF HIDES AND SKINS, RAW AND TANNED.—

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Goat-skins, pounds . . . | 53,968,385 | 46,747,029 | 49,868,020 | 64,923,487 | 69,728,945 |
| Valued at . . . . . . | $10,894,845 | $10,304,395 | $11,328,162 | $15,776,601 | $18,488,326 |
| All other skins, pounds . | 170,977,644 | 163,650,982 | 156,232,824 | 180,851,129 | 197,361,805 |
| Valued at . . . . . . | $15,067,104 | $20,215,782 | $16,534,864 | $21,292,331 | $23,499,717 |
| Skins for morocco leather, valued at . . . . . | $3,728,255 | $3,145,989 | $3,716,259 | $3,081,770 | $2,455,332 |
| Upper leather, valued at. | $2,351,156 | $2,384,263 | $2,410,862 | $2,210,937 | $2,470,841 |
| Gloves of kid or other leather, valued at . . | $6,463,872 | $6,763,082 | $6,486,813 | $5,384,168 | $5,398,125 |

The following figures of importations of goat-skins at the ports of New York and Philadelphia, with localities from which they are brought, were presented to the "Morocco Manufacturers' National Association" at their annual meeting, July 11, 1895.

ARRIVALS AT NEW YORK.

| | 1892. First 6 months. Skins. | 1893. First 6 months. Skins. | 1894. First 6 months. Skins. | 1895. First 6 months. Skins. |
|---|---|---|---|---|
| Mexican . . . . . . | 937,872 | 910,201 | 896,400 | 773,000 |
| Texas and Mexican frontier . . . . . . | 493,400 | 261,700 | 309,400 | 427,100 |
| Curaçoa . . . . . . . | 257,300 | 413,300 | 428,800 | 418,500 |
| Maracaibo, Rio Hacha, Porto Cabello, and Laguayra . . . . . | 59,500 | 63,600 | 70,300 | 60,300 |
| Brazil . . . . . . . . | 1,504,200 | 1,231,200 | 1,371,000 | 1,613,700 |
| Buenos Ayres . . . . | 436,200 | 273,000 | 594,600 | 373,200 |
| Payta . . . . . . . . | 145,500 | 409,750 | 478,000 | 208,800 |
| Oajaca . . . . . . . | 73,978 | 94,236 | 51,600 | 59,000 |
| West Indies . . . . . | 82,125 | 94,500 | 78,625 | 72,500 |
| Bogota . . . . . . . | 19,680 | 37,920 | 30,000 | 13,440 |
| Angostura . . . . . . | 2,460 | 6,450 | 4,360 | 1,890 |
| European, Asiatic, and African . . . . . . | 2,899,000 | 2,868,300 | 2,061,300 | 4,225,375 |
| Arabian . . . . . . . | 382,000 | 1,565,250 | 1,667,500 | 1,422,750 |
| Calcutta . . . . . . . | 2,363,500 | 2,614,000 | 2,152,500 | 3,497,000 |
| | 10,156,715 | 10,843,407 | 10,194,385 | 13,166,555 |

AT PHILADELPHIA.

| | 1892. | 1893. | 1894. | 1895. |
|---|---|---|---|---|
| European, Asiatic, and African . . . . . . | 875,700 | 1,347,300 | 598,900 | 1,490,875 |
| Arabian . . . . . . . | 45,000 | 14,500 | 34,250 | 44,000 |
| Calcutta . . . . . . . | 639,000 | 804,500 | 157,500 | 862,000 |
| | 1,559,700 | 2,166,300 | 790,650 | 2,396,875 |

5. UNITED STATES EXPORTATIONS OF LEATHER.—

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Sole-leather, pounds . . . | 45,364,349 | 41,818,503 | 38,384,314 | 37,813,019 | 37,120,912 |
| Valued at . . . . . . | $6,919,372 | $7,474,021 | $6,510,404 | $6,644,553 | $6,280,904 |
| Buff, grain, and upper leather, valued at. | $6,038,940 | $9,273,315 | $9,107,053 | $10,293,430 | $12,353,995 |
| All other leather, valued at | $682,241 | $1,017,649 | $813,798 | $858,421 | $1,090,574 |

6. ENGLISH IMPORTATIONS OF HIDES.—

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Hides, dry, cwt. . . . . . | 491,547 | 369,063 | 556,587 | 542,454 | 446,285 |
| Valued at . . . . . . | £1,153,757 | £905,427 | £1,413,166 | £1,455,806 | £1,148,652 |
| Hides, wet, cwt. . . . . . | 771,133 | 604,728 | 638,658 | 694,057 | 764,240 |
| Valued at . . . . . . | £1,650,369 | £1,319,501 | £1,336,988 | £1,450,260 | £1,641,514 |

*English Exportations of Leather.*—

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Leather, unwrought, cwt. | 159,037 | 138,069 | 157,892 | 159,399 | 155,002 |
| Valued at . . . . . . | £1,422,747 | £1,279,702 | £1,389,811 | £1,422,508 | £1,473,294 |

7. EXPORTATIONS OF GLUE FROM THE UNITED STATES.—

| | 1895. | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|---|
| Glue, pounds . . . . . . . | 1,178,828 | 1,760,470 | 1,400,863 | 2,318,711 | 2,368,087 |
| Valued at . . . . . . . . | $114,493 | $166,930 | $132,581 | $209,441 | $222,072 |

# CHAPTER XI.

## INDUSTRIES BASED UPON DESTRUCTIVE DISTILLATION.

DESTRUCTIVE distillation has been defined as "the decomposition of a substance in a close vessel in such a manner as to obtain liquid products." It must be observed here that the word product is used to indicate something not originally present in the substance distilled. A body may be obtained in the liquid distillate which has merely been driven over by heat and which already existed in the original material in physical or mechanical admixture. Such a body is, to speak exactly, an *educt* and not a *product*.

The substances which are submitted to destructive distillation are in the main solids, as most classes of liquids are capable when heated with care of volatilization without decomposition, although such liquids as fatty oils, glycerine, etc., are decomposed if distilled under normal atmospheric pressure. (The cracking of petroleum is another illustration of destructive distillation of a liquid purposely brought about.) With solids, on the other hand, it is the exception rather than the rule to find one capable of melting and vaporizing unchanged in composition when distilled under normal atmospheric pressure. The same solid, moreover, if of at all complex molecular composition, may decompose quite differently and yield different sets of products according to the conditions which govern the distillation. The most important of these modifying conditions is that of temperature. "Low temperature" distillation and "high temperature" distillation as practised upon the same material (wood or coal, for example) may yield quite different results. The physical condition or mechanical subdivision of the substance also has an influence, although a subordinate one, upon the nature of the products. Solids, upon the destructive distillation of which important industries are founded, are wood, coal, shales, bones, and animal refuse. The distillation of shale has already been considered in connection with the mineral oil industry. (See p. 27.) The other industries will now be noted in succession.

## A. DESTRUCTIVE DISTILLATION OF WOOD.

### I. Raw Materials.

1. COMPOSITION OF WOOD.—The wood which is to be destructively distilled is composed, we may say in general terms, of woody fibre and plant-juice or sap, which is an aqueous solution of the substances, both nitrogenous and non-nitrogenous, which serve as the food for the living plant. The woody fibre is made up primarily of cellulose, which is in part changed into "lignin," as the incrusting substance is called. In percentage composition this latter substance differs from the pure cellulose in containing more carbon and less oxygen and hydrogen. The amount of incrusting material varies, being more abundant in hard and heavy varieties than in light and soft kinds, and wood which contains it in the largest proportion

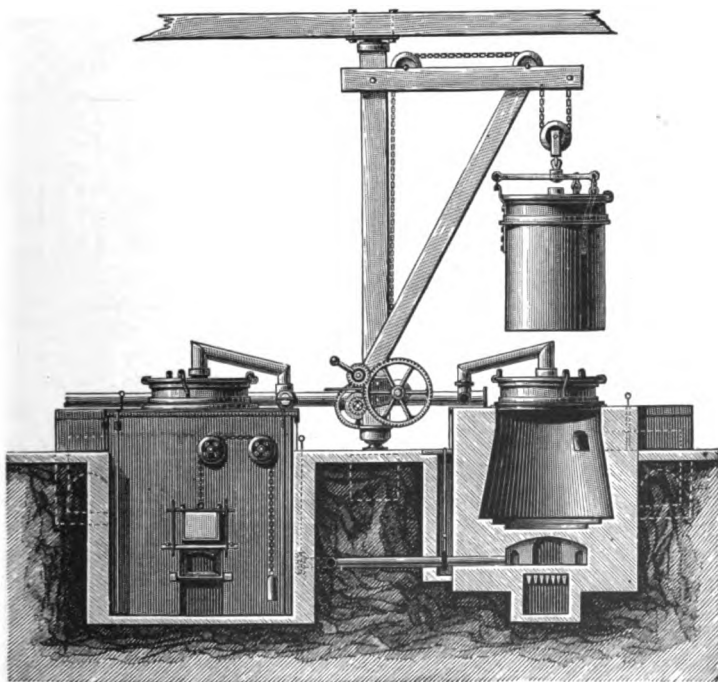
gives the most acid and naphtha on distillation. The amount of water present in wood also varies not only according to the season of the year, but also quite widely in different woods cut at the same season. Thus, the following table of Schübler and Hartig shows the percentage of water of different trees taken at the period of minimum amount:

| | Per cent. of water. | | Per cent. of water. |
|---|---|---|---|
| Beech | 18.6 | Horsechestnut | 38.2 |
| Willow | 26.0 | Pine | 39.7 |
| Maple | 27.0 | Alder | 41.6 |
| Elder | 28.3 | Elm | 44.5 |
| Ash | 28.7 | Lime | 47.1 |
| Birch | 30.8 | Lombardy poplar | 48.2 |
| White hawthorn | 32.3 | Larch | 48.6 |
| Oak | 34.7 | White poplar | 50.6 |
| White fir | 37.1 | Black poplar | 51.8 |

2. EFFECT OF HEAT UPON WOOD.—The effect of heat upon wood in the absence of air is a matter which is to be carefully noted as throwing light upon the results obtained in destructive distillation. It of course differs radically from the result of heating with free contact of air. Violette found that when wood was carefully and slowly heated no decomposition occurred under 150° C., water only being given off; between 150° and 160° C. the loss was two per cent. of the weight of the water-free wood; between 160° and 170° C., 5.5 per cent.; between 170° and 180° C., 11.4 per cent., and so on until at 280° C. 63.8 per cent. of volatile products had been driven off and 36.2 per cent. only of the water-free wood remained in the retort. The products given off in this period of heating between 150° and 280° are the valuable liquid products known as pyroligneous acid (acetic acid and its homologues), wood-naphtha or methyl alcohol, methyl acetate, acetone, furfurol, the mixture of phenols known collectively as "wood-creosote," and other bodies of empyreumatic and tarry odor. These bodies differ, as will be seen later in very important respects, from coal-tar products. Above 280° C., the decomposition proceeds somewhat differently, hydrocarbons, both gaseous and liquid, being formed. The additional percentage of loss by weight between 280° and 350° C. is only 6.5 per cent. of the water-free wood, but it makes from eighty to ninety volumes of gas. The decomposition continues from 350° to 430° C., when the total loss by weight amounts to eighty-one per cent. of the water-free wood. The products obtained within these limits of temperature are largely solid hydrocarbons like paraffin and high temperature products like benzene and toluene, naphthalene, phenol and cresol. From 430° to 1500° C. the additional loss of weight is only 1.7 per cent. We may sum up these results by saying that three periods may be distinguished broadly for this decomposition of wood by heat: first, from 150° to 280° C., the period of watery acid products; second, from 280° to 350° C., the period of gaseous products; and, third, from 350° to 430° C., the period of liquid and solid hydrocarbons. Violette found also great difference in the results according as the temperature was slowly raised or as the wood was rapidly brought up to a higher heat. Thus, one hundred parts by weight of wood slowly heated so that the temperature of 432° C. was only reached after six hours left 18.87 parts of charcoal, while one hundred parts of the same wood put into a retort previously heated to 432° C. left only 8.96 parts by weight of charcoal.

## II. Processes of Manufacture.

1. Distillation of the Wood.—The primitive method of distilling wood devised by the charcoal-burners, in which the wood was piled up in large heaps covered in by clay and turf so as to form a circular dome-shaped mound, is still followed in some heavily-wooded districts. Of course the charcoal is the only product sought in this case, and the gaseous and liquid products of the distillation are allowed to escape. In Russia and Sweden the charcoal-burning in mounds is now frequently combined with the collection of the tar, which as it condenses is made to flow through inclined troughs, and is drawn off from below. In this way the valuable birch-bark tar (see p. 334) and kienoel (Russian turpentine oil) are obtained. For a proper collection of all the products of the destructive distillation of wood, however, it is essential that the distillation be carried out in retorts provided with proper condensation apparatus. These retorts may be either set in horizontal or vertical position, and may be either fixed or capable of removal for emptying and re-charging. It is found convenient in large works where it is desirable to carry on the distillation continuously to have a series of retorts connected with one and the same condensation apparatus and

Fig. 101.

heated by the same flues. Such an arrangement of retorts is shown in Fig. 101. This arrangement allows of the removal and re-charging of a single retort without interrupting the working of the others. The heating should be conducted slowly at first so that the maximum yield of the low temperature products, acetic acid and methyl alcohol, may be obtained, then increased until the gas comes off freely, and at the end of this stage of

the decomposition again strengthened to drive over the high temperature products characteristic of the last period of distillation. As the maximum temperature needed is beyond the record of the mercury thermometer, a pyrometer can be used or a small bar of metallic antimony which melts at 432° C. taken as indicator. Superheated steam has also been used as a means of accurately controlling the application of heat in the distillation, and it is said that the majority of European works manufacturing charcoal for gunpowder purposes use this method of distillation. The liquid which runs off from the condenser is at first wax-yellow in color, but becomes dark-colored, reddish-brown, and eventually nearly black and quite turbid. When allowed to stand at rest it soon separates in two sharply distinct layers,—the lower one of a thick tar, dark or perfectly black in color, and the upper one, which is much the larger in amount, is the crude pyroligneous acid and is reddish-yellow or reddish-brown in color. A light film of oil often covers, in part at least, this watery layer and represents the benzene hydrocarbons produced. We have already noted the fact that the yield of liquid products was affected greatly by the temperature used for distillation. Different varieties of wood also vary somewhat in the results obtained, even when distilled under the same conditions of temperature. This is illustrated in the following few examples: *

| | Charcoal. | Tar. | Crude pyroligneous acid. | Containing actual acid. | Gases. |
|---|---|---|---|---|---|
| Red beech, slowly heated | 26.7 | 5.9 | 45.8 | 5.2 | 21.7 |
| Red beech, rapidly heated | 21.9 | 4.9 | 39.5 | 3.9 | 33.8 |
| Birch, slowly heated | 29.2 | 5.5 | 45.6 | 5.6 | 19.7 |
| Birch, rapidly heated | 21.5 | 3.2 | 39.7 | 4.4 | 35.6 |
| Oak, slowly heated | 34.7 | 3.7 | 44.5 | 4.1 | 17.2 |
| Oak, rapidly heated | 27.7 | 3.2 | 42.0 | 3.4 | 27.0 |
| Pine, slowly heated | 30.3 | 4.4 | 41.0 | 2.7 | 24.4 |
| Pine, rapidly heated | 24.2 | 9.8 | 42.0 | 2.4 | 24.1 |

Beech-wood and foliage trees in general yield distinctly more acid than coniferous trees, but the latter yield more tar of terebinthinate character. The figures given above, it must be remembered, however, were gotten in experiments with small portions. In practice, working with larger quantities, the yield of several of the products is notably larger. The yield of wood-spirit, or methyl alcohol, varies from five-tenths to one per cent. of the weight of the dry wood.

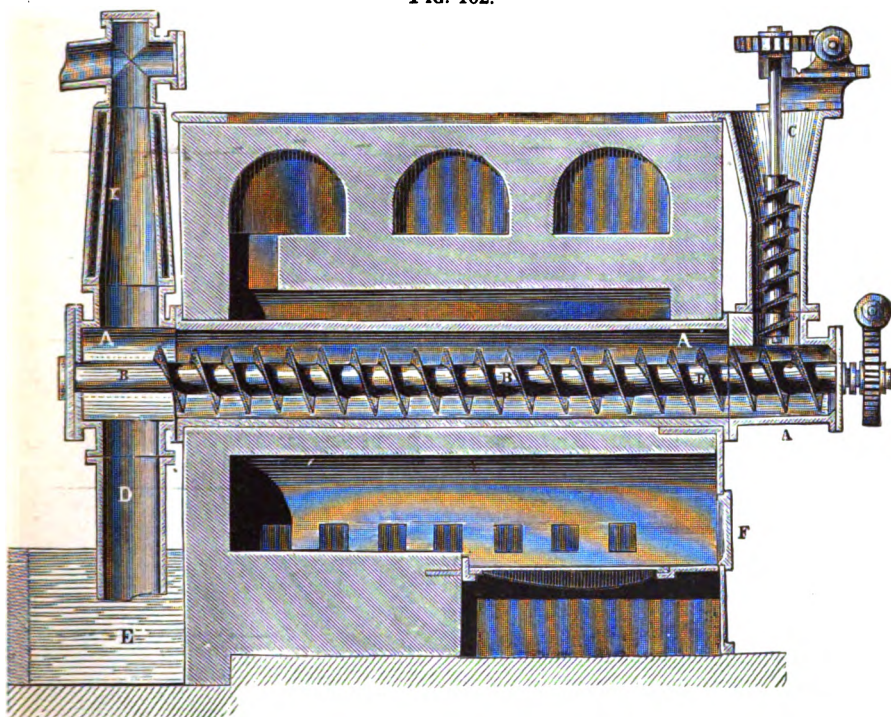
The emptying of the retorts, if done as intended while the charcoal is yet glowing, involves the use of air-tight pits into which the charcoal can be emptied from the retorts and immediately covered with moist charcoal-powder to prevent loss by combustion. A form of apparatus for distilling the sawdust so abundantly produced in wood-working processes has been devised by Halliday, of Salford, England, and is said to work satisfactorily in practice. It is shown in Fig. 102. It consists of a horizontally placed cylindrical retort, *A*, within which revolves an endless screw, *B*. The sawdust is regularly fed in through the vertical pipe *C*, and falling upon the screw is kept moving at a uniform speed along the entire length of the heated retort. At the farther end the vapors and gaseous products of the

* Ost, Lehrbuch der technische Chemie, p. 294.

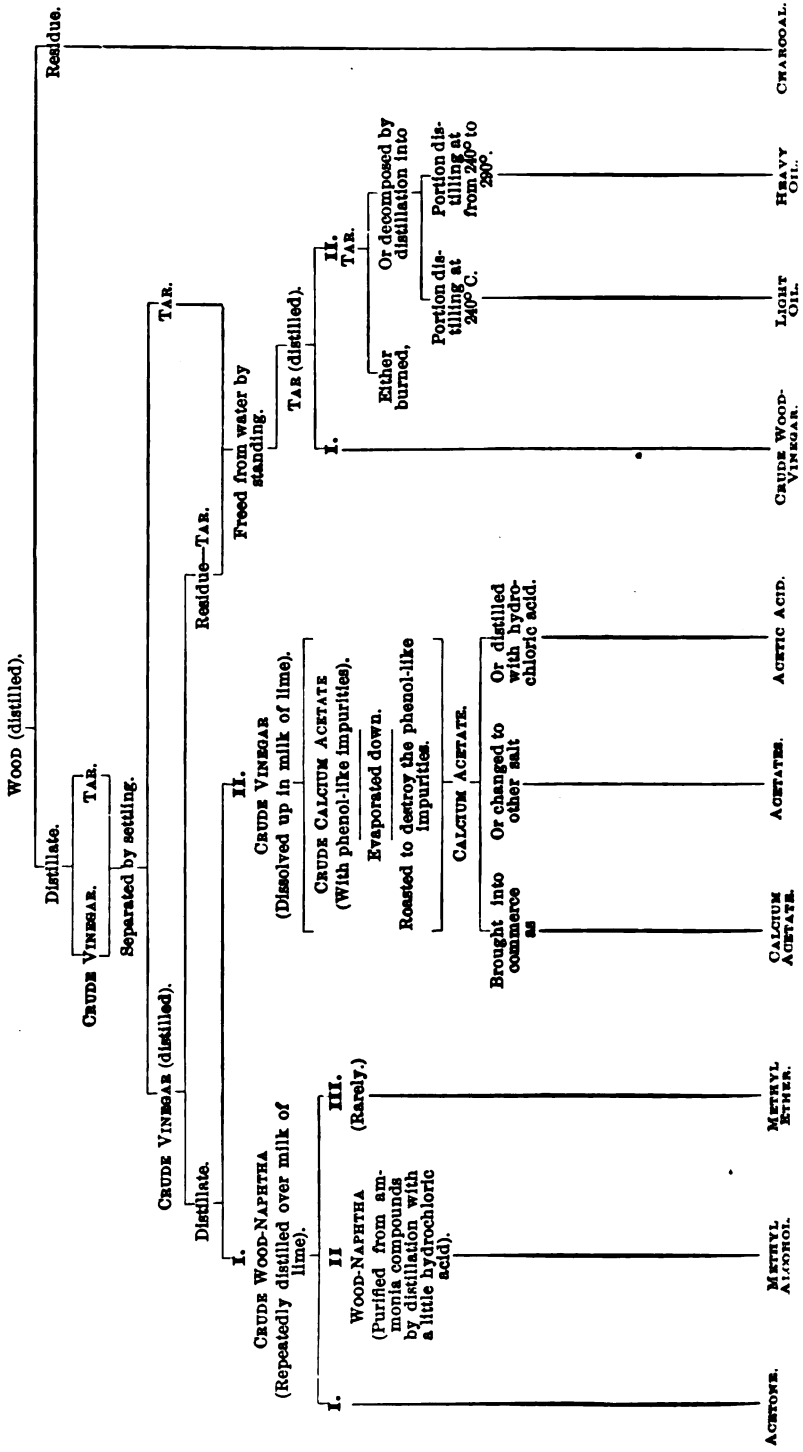
distillation escape through an ascending pipe, *K*, leading to the condenser, while the powdered charcoal drops through the pipe *D* into water, where it is at once quenched.

A general view of the products of the distillation of wood and their subsequent treatment is given in the accompanying diagram taken from Post.*

2. Treatment and Purification of the Crude Wood-vinegar.—The brown aqueous solution poured off from the tarry layer (see above) has a strong empyreumatic odor, and contains, besides the acetic acid, methyl alcohol, acetone, and homologous ketones, allyl alcohol, homologues of acetic

Fig. 102.

acid (such as formic, propionic, butyric, and valerianic acids), methyl acetate, acetate of ammonia and of methylamine, aldehyde, furfurol, phenols, and other empyreumatic and tarry bodies. It is not used in its crude condition except in the preparation of the crude pyrolignite of iron (*iron-liquor*) or in limited amount for impregnating wood. The first step towards purification is to separate the *wood-naphtha* (the fraction containing the methyl alcohol acetone and methyl acetate) from the *wood-vinegar* (crude acetic acid), which is done by distillation. Two procedures are possible here. Either to neutralize the crude pyroligneous acid with milk of lime and then distil off the volatile constituents only, using an iron still, or to distil the crude pyroligneous acid from a copper still without neutralizing with lime. In the former case, while the wood-naphtha distils off, the tarry impurities of the crude pyroligneous acid remain with the lime salt in the still, and on evap-

* Post, Chem. Technologie, p. 78.

## PRODUCTION AND TREATMENT OF WOOD-TAR.

oration a dark mass is obtained known as "brown acetate of lime." In the latter case, after catching the wood-naphtha distillate, the receiver is changed and the crude acetic acid is also collected freed to a considerable extent from tarry matter, so that on neutralizing with milk of lime and evaporating the product is a lighter salt known as "gray acetate of lime." The latter process is now more generally in use. The solution of the calcium acetate is evaporated in iron pans; the phenols and tarry products which volatilized with the acetic acid separate largely as scum and may be skimmed off, so that the residue of the evaporation is much purer than the product of the other method mentioned above.

If the brown acetate of lime has been obtained and is to be further worked for acetic acid, it is found necessary to roast it at a temperature not exceeding 250° C. so as to drive off as much of the tarry impurity as possible without decomposing any of the acetate. If, on the other hand, the gray acetate is taken, it is distilled from copper retorts with concentrated aqueous hydrochloric acid, taking care to avoid an excess. The acetic acid distils over between 100° and 120° C., is clear in color and has only a slight empyreumatic odor. Its specific gravity usually ranges from 1.058 to 1.061, and it contains about fifty per cent. of pure acetic acid. If some water is added with the hydrochloric acid so that the distilled acetic acid is more dilute it tends to give a purer product, as the liberated acetic acid cannot decompose any of the calcium chloride before coming over. A good proportion is said to be one hundred parts of acetate of lime, ninety tc ninety-five of hydrochloric acid of 1.160 specific gravity, and twenty-five parts of water. The acetic acid so obtained has a slight empyreumatic odor. It may be freed from this by distilling with from two to three per cent. of potassium bichromate, or by filtration through freshly ignited wood charcoal.

The brown acetate of lime usually contains about sixty-eight to sixty-nine per cent. of pure acetate, while the gray acetate contains from eighty-five to eighty-six per cent. of true acetate.

In recent years it has been found practicable to prepare pure acetic acid from the crude pyroligneous acid by making the sodium salt instead of the lime salt. The sodium salt allows of purifying by recrystallization, and can also be fused without decomposition. Glacial acetic acid is generally made by distilling the anhydrous and fused sodium acetate with concentrated sulphuric acid.

Rohrmann has recently developed a process by which it is possible to make ninety per cent. or even glacial acetic acid direct from the crude acetate of lime in one operation. He uses a column still provided with Lunge-Rohrmann plates, over which concentrated sulphuric acid is made to trickle. This meets the ascending acetic vapors and dehydrates them. They pass over into a condenser, while the empyreumatic vapors are drawn off by a warm-air current which connects with the column. When hydrochloric acid is used to decompose the acetate the resulting acetic acid can be brought to eighty per cent.; when sulphuric acid is used, one hundred per cent. acid can be obtained.

3. Purification of the Crude Wood-spirit.—The wood-spirit forms the first fraction when the crude pyroligneous acid is distilled, and amounts to perhaps one-sixth of the latter in bulk. It is usual to collect, however, until the hydrometer reading of the distillate, which begins at about .900, has risen to 1.000 or a little beyond. This distillate forms a greenish-yellow liquid of unpleasant odor and contains many impurities

besides the acetone and methyl acetate, the chief substances which are present with the methyl alcohol. Milk of lime is first added and allowed to stand with the liquid for several hours. The mixture heats up quite distinctly as the lime combines with any free acid and begins to decompose the methyl acetate and other ethereal compounds of acetic acid, small quantities of ammonia often being given off. It is then distilled by connecting it with a column rectifying apparatus. (See p. 220.) The distillate thus obtained, of about .816 specific gravity, is colorless at first but gradually darkens in color, and if diluted with water becomes milky from separated oily hydrocarbons and ketones. It is therefore diluted down with water to about .935 specific gravity and allowed to stand until this oily impurity rises to the top in a distinct layer. The diluted spirit is again distilled over lime once or twice with a rectifying column and so brought to ninety-eight or ninety-nine per cent. strength. The acetone impurity, however, is not removed by any of these rectifications, as the boiling-point of acetone (56.4° C.) and methyl alcohol (55.1° C.) do not allow of their separation in this way. To remove the acetone a number of methods have been proposed. The methyl alcohol may be converted into the solid chloride of calcium compound, or the oxalate of methyl and the acetone having been removed by careful heating, the methyl compound is decomposed by water or alkali. Or the methyl alcohol is distilled over chloride of lime, which reacts with the acetone to form chloroform. The passing in of chlorine in order to convert the acetone into high-boiling chloracetones, which are then separated from the methyl alcohol by distillation, has also been proposed.

4. TREATMENT OF THE WOOD-TAR.—The tar which has separated from the crude pyroligneous acid by settling, and that which has risen and been skimmed off in the neutralizing of the acid, are united and submitted to distillation in horizontally-placed iron retorts, which are set at a slight inclination. At first acid-water comes over, then light oils, and finally heavy oils until no more will distil. The pitchy residue is run out while hot, so that it does not adhere to the walls of the retort. The relative amounts of the several fractions from the tar depend upon the nature of the wood used in the original distillation and upon the way that distillation has been carried out. Hard woods usually give a tar which, according to Vincent, when redistilled yields as follows:

| | |
|---|---|
| Aqueous distillate (wood-spirit and pyroligneous acid) . . | 10 to 20 per cent. |
| Lighter oily distillate (specific gravity .966 to .977) . . . | 10 to 15 " " |
| Heavy oily distillate (specific gravity 1.014 to 1.021) . . . | 15 " " |
| Pitch . . . . . . . . . . . . . . . . . . . . . . . . | 50 to 65 " " |

The oily distillates are washed with weak soda to remove adhering acid and then carefully rectified, when the oils coming over under 150° C. are collected for solvent and varnish-making purposes, those between 150° and 250° C. collected as creosote oils, and those above 250° C. used for burning oils.

The creosote oil, which is the most valuable part, is thoroughly agitated with strong caustic soda solution, the aqueous layer drawn off, mixed with sulphuric acid, and allowed to stand for a time at rest, when the creosote oil separates out. This is best driven off by steam distillation and again rectified finally from glass retorts.

Stockholm tar, so largely used in ship-building, is the product of a rude distillation of the resinous wood of the pine.

North Carolina pine-tar is also the product of a distillation of the pine. The billets of pine-wood are piled in heaps like a charcoal-burner's mound,

though not so large, covered in with clay and turf, and lighted from the top. The resin or tar distils downward and runs off through inclined troughs previously fixed for it. It is obvious that the composition of both the Stockholm and the North Carolina tar differs notably from that of wood-tar distilled in retorts from hard woods. This composition will be referred to later.

## III. Products.

1. Pyroligneous Acid and Products therefrom.—The crude acid as obtained in the distillation is a clear liquid of reddish-brown color and strong acid taste, with a peculiar penetrating odor described as empyreumatic, and now known to be due largely to the furfurol it contains. It possesses a specific gravity of from 1.018 to 1.030 and contains from four to seven per cent. of real acetic acid. *Pyrolignite of iron* (iron or black liquor) is a solution of ferrous acetate with some ferric acetate, prepared by acting upon scrap-iron with crude pyroligneous acid. It forms a deep-black liquid, and is concentrated by boiling to 1.120 specific gravity, when it contains about ten per cent. of iron. It is extensively used by calico-printers. *Brown and gray acetate of lime* have been already referred to. Other technically important acetates are *lead acetate* (sugar of lead), used in the preparation of the alum mordants and the lead pigments; *copper acetate*, the basic salt of which is known as "verdigris;" *aluminum acetate*, the solution of which is used in calico-printing under the name of "red liquor."

*Pure acetic acid* is a colorless acid liquid with pungent smell and taste. It crystallizes when chilled in large transparent tablets, melting at 16.7° C., whence the name "glacial acetic acid." Its specific gravity at 15° C. is 1.0553, and it boils under normal pressure at 119° C.

2. Methyl Alcohol and Wood-spirit.—As before stated, crude wood-spirit is a complex liquid and contains many impurities. The percentage of real methyl alcohol may rise to ninety-five per cent., but more generally ranges from seventy-five to ninety per cent. Some impure wood-naphthas go much lower, however, than this. A large percentage of acetone does not interfere with its use as a solvent for resins and for varnish-making, but does interfere with its use in the aniline-color industry, where a very pure methyl alcohol is needed for the manufacture of dimethyl aniline. The methods of freeing methyl alcohol from the two chief impurities, methyl acetate and acetone, have already been referred to. Pure methyl alcohol has a purely spiritous odor, a specific gravity of .7995 at 15° C., and boils at 55.1° C. It is miscible in all proportions with water, ordinary alcohol, and ether.

3. Acetone.—This substance is of interest as always produced in the distillation of wood, and hence present in the crude wood-spirit. The acetates yield it as the chief product when submitted to dry distillation, and the vapors of acetic acid distilled over porous baryta at a temperature of from 350° C. to 400° C., it has been found by Dr. Squibb, will also readily yield acetone. One hundred kilos. of forty per cent. acid will give from twelve to thirteen kilos. of acetone. At present it is made on a large scale by distilling the gray acetate of lime in iron stills provided with mechanical agitation at a temperature of about 290° C. When purified, it is a colorless liquid of peculiar ethereal odor and burning taste, and, like methyl alcohol, is miscible in all proportions with ether, alcohol, and water. It is an excellent solvent for resins, gums, camphor, fats, and pyroxylin, or gun-

cotton. It does not form a compound with dry calcium chloride, and can thus be separated from methyl alcohol when in admixture with this latter. Chlorine and iodine in the presence of an alkali react with acetone to form chloroform and iodoform.

4. CREOSOTE.—Wood-tar creosote is a strongly refracting liquid, which is colorless when freshly distilled but gradually acquires a yellow or brown color. It has a smoky aromatic odor, which is very persistent and is quite distinct from that of carbolic acid. It has a specific gravity ranging from 1.030 to 1.080, and boils between 205° and 220° C. It is a powerful antiseptic, and is largely used to preserve meats, etc. It differs from coal-tar creosote in containing relatively little common phenol (carbolic acid) and relatively large amounts of higher phenols, such as phlorol, $C_8H_9.OH$, guaiacol, $C_7H_7O.OH$, and creosol, $C_8H_9O.OH$.

5. PARAFFINE.—This mixture of solid hydrocarbons, as already said, occurs in the higher boiling distillate gotten from wood. It is of interest to recall that paraffine was first discovered by Reichenbach in beech-wood tar. At present, however, the extraction of paraffine from wood-tar is not to be thought of because of the cheapness of its production from petroleum and bituminous shales. It has been already described under the chapter on Petroleum. (See p. 31.)

6. CHARCOAL.—We have already shown in the table of results of slow and rapid distillation of wood (see p. 350) that the relative amount of charcoal depends upon the manner of heating, being larger with gradual application of heat and smaller with rapid heating. The properties and chemical composition of the charcoal are similarly dependent upon the temperature to which the wood is heated. Wood is stated to become brown at 220° C., at 280° C. it becomes a deep brownish-black and begins to be friable, and at 310° C. forms an easily friable black mass taking fire easily. That prepared at higher temperatures is harder and less readily ignited, and it eventually becomes graphitic and rings with a metallic sound when struck. The accompanying table from Violette shows the gradual change in the composition of charcoal prepared at different temperatures from the same kind of wood (buckthorn):

| | Heated to | Carbon, per cent. | Hydrogen, per cent. | Oxygen, nitrogen, and loss. | Ash, per cent. |
|---|---|---|---|---|---|
| Dry wood . . . . . . . | 150° C. | 47.51 | 6.12 | 46.29 | 0.08 |
| Charred wood . . . . . | 260° C. | 67.85 | 5.04 | 26.49 | 0.56 |
| Red charcoal . . . . . . | 280° C. | 72.64 | 4.70 | 22.10 | 0.57 |
| Brown charcoal . . . . | 320° C. | 73.57 | 4.83 | 21.09 | 0.52 |
| Dull black charcoal . . . | 340° C. | 75.20 | 4.41 | 19.96 | 0.48 |
| Lustrous black charcoal . | 432° C. | 81.64 | 1.96 | 15.25 | 1.16 |
| Extreme white heat . . | 1500° C. | 96.52 | 0.62 | 0.94 | 1.95 |

## IV. Analytical Tests and Methods.

1. ASSAY OF PYROLIGNEOUS ACID AND CRUDE ACETATES.—The crude pyroligneous acid, as before stated, contains from four to seven per cent. of real acetic acid. Its strength may be ascertained by titration with standard alkali, using phenol-phthalëin as an indicator. If the liquid is too dark to allow of the end reaction being readily seen, it can be diluted sufficiently, as the reaction will still be sufficiently delicate. In the absence

of sulphates in the sample, the acetic acid can be determined by adding excess of pure precipitated barium carbonate to the solution, filtering, and determining the barium in the filtrate by the aid of sulphuric acid.

As the pyroligneous acid is largely converted into calcium acetate in the process of purifying, the analysis of the brown or gray acetate of lime as a common commercial product becomes of some importance. This commercial acetate may contain from sixty-five to eighty per cent. of true acetate of lime, with carbonate of lime, so-called "tar-lime," and empyreumatic matter as chief impurities. The acetic acid determination may be made by different methods, but the most accurate according to the experience of the author is the distillation method, as suggested by Stillwell and Gladding. One gramme of the sample of acetate of lime is placed in a small distillation bulb or flask with a long neck, a little distilled water added, and then a solution of five grammes of glacial phosphoric acid dissolved in ten cubic centimetres of water. The flask is then heated to distil off the acetic acid, care being taken to avoid spurting and mechanical carrying over of any of the phosphoric acid. When the contents have nearly gone to dryness, some twenty-five cubic centimetres of distilled water are introduced and the distillation repeated. If this is done some three or four times, the distillate will be found to be free from acid reaction. The combined distillate is then brought to definite volume and titrated with decinormal soda solution, using phenolphthaleïn as indicator.

2. DETERMINATION OF METHYL ALCOHOL IN COMMERCIAL WOOD-SPIRIT.—But one method, and that not capable of the most accurate working, is at present available. Five cubic centimetres of the sample of wood-spirit are allowed to drop slowly upon fifteen grammes of phosphorous di-iodide placed in a small flask of some thirty cubic centimetres capacity. This is connected with an inverted condenser and cooled externally while the reaction takes place. Five cubic centimetres of a solution of one part iodine in one part of hydrogen iodide of 1.7 specific gravity is then added and the mixture gently digested for a quarter of an hour, when the condenser having been turned downward the iodide of methyl formed is distilled off. It is collected in a graduated tube divided into one-tenth cubic centimetres, washed with some fifteen cubic centimetres of water with vigorous agitation, allowed to settle, and the volume read off. Five cubic centimetres of pure and perfectly dry methyl alcohol should give 7.45 cubic centimetres of iodide of methyl.

3. DETERMINATION OF THE ACETONE IN COMMERCIAL WOOD-SPIRIT.—This may be done by either the Kraemer and Grodzki gravimetric method or the Messinger volumetric method, both of which depend upon its quantitative conversion in the presence of iodine and caustic alkali into iodoform. In the former case, one cubic centimetre of the sample of wood-spirit is mixed with ten cubic centimetres of a double normal solution of caustic soda (eighty grammes to the litre), and to the mixture, after thorough agitation, is added five cubic centimetres of a solution containing two hundred and fifty-four grammes of iodine and three hundred and thirty-two grammes of potassium iodide to the litre. The iodoform which separates on agitation is dissolved by the addition of ten cubic centimetres of ether free from alcohol. An aliquot portion of the ethereal layer is then pipetted off into a tared watch-crystal, and the iodoform remaining after evaporation is weighed. Three hundred and ninety-four parts of iodoform correspond to fifty-eight parts of acetone. More accurate is the Messinger volumetric process. In this, twenty cubic centimetres (or thirty cubic centimetres in

samples rich in acetone) of normal potash solution and one or two cubic centimetres of the wood-spirit in question are shaken together in a stoppered 250-cubic-centimetre flask and a known quantity (twenty or thirty cubic centimetres) of a one-fifth normal iodine solution added. The mixture is shaken until the supernatant liquid clears perfectly on momentary standing, hydrochloric acid of 1.025 specific gravity is added in amount equal to the potash solution before used, and excess of decinormal sodium thiosulphate run in. Starch paste is then added, and the excess of sodium thiosulphate titrated with one-fifth normal iodine solution. If $r$ be the volume in cubic centimetres of the iodine solution required to combine with the acetone, and $n$ the volume in cubic centimetres of the methyl alcohol taken, then the quantity of acetone by weight in one hundred cubic centimetres of the sample is equal to $\frac{r \times .193345}{n}$.

4. QUALITATIVE TESTS FOR WOOD-TAR CREOSOTE.—Allen * enumerates the following tests as characteristic of wood-tar creosote or as sufficing to distinguish it from coal-tar creosote: (1) An alcoholic solution of wood-creosote should not give any coloration whatever (neither blue nor reddish) with baryta-water; (2) wood-tar creosote is practically insoluble in strong ammonia; (3) wood-tar creosote is also distinguished from the coal-tar acids by its reaction with an ethereal solution of nitrocellulose. Shaken with half its measure of collodion solution carbolic acid coagulates the gun-cotton to a transparent jelly. Creosote does not precipitate the nitrocellulose from collodion but mixes perfectly with the ethereal solution; (4) wood-tar creosote is sharply distinguished from the coal-tar acids by its insolubility in absolute glycerine (specific gravity 1.26), whether one, two, or three times its volume of that liquid be employed.

## *B.* DESTRUCTIVE DISTILLATION OF COAL.

### I. Raw Materials.

Probably the most important industry involving the destructive distillation of coal is the manufacture of illuminating gas. The classes of coals employed for the purpose are confined to those varieties which are bituminous in their nature, yielding when distilled volatile hydrocarbons in varying quantity. The uncombined or "fixed carbon," with the mineral constituents originally present in the coal, remaining after the distillation comprise coke.

*Bituminous Coals* have the property, not possessed by the anthracites, of softening and apparently fusing when subjected to a temperature below that at which combustion would take place. This fusion indicates the commencement of destructive distillation, when both solid, liquid, and gaseous carbon compounds are formed. Bituminous coal is essentially a coking coal, and as such is, to a very great extent, employed in the coking regions of Western Pennsylvania. It is black or grayish-black in color, of a resinous lustre, and somewhat friable, being easily broken into cubical fragments of more or less regularity; upon ignition it burns with a yellow flame. When it is heated to bright redness in retorts or ovens, free from the access of air, the volatile matter, before mentioned, carbon compounds of hydrogen and of oxygen, with water, pass off. Coals having a large percentage of hydrogen will yield more volatile substances at the temperature of distillation

* Commercial Organic Analysis, 2d ed., vol. ii. p. 568.

and less carbonaceous residue than others which may contain less hydrogen and more carbon,—approaching anthracite in composition.

*Coking and Non-coking Coals* are quite similar in chemical composition; the coking varieties contain less volatile matter, however, than the non-coking; the latter do not possess the property of fusing to a compact "coky" mass, but retain their original form, and yield a coke which has no commercial value unless it is obtained from large pieces of the coal.

*Cannel Coal* is much more compact than gas or coking coals, duller in appearance, possessing a grayish-black to brown color, and burning with a clean candle-like flame. It does not soil the hands, and is not readily fractured. It is capable of taking a high polish, and can be cut or turned into articles for use or ornamentation. Cannel coal occurs in large quantities in West Virginia, and near Glasgow, Scotland, in Lancashire, England, and at other localities. Destructively distilled, it yields a larger amount of volatile matter and ash, with much less coke, than the bituminous coals.

*Brown Coal, or Lignite,* appears to occupy an intermediate position between the bituminous coals and wood. It retains the ligneous structure of the material from which it is formed,—hence the name *Lignite.* The vegetable remains in a great many cases are quite distinct. The color varies from yellowish-brown in the earthy, to black in the more compact, coal-like varieties. The percentage of carbon contained is low, fifty to eighty per cent., though rarely exceeding seventy per cent., while the hydrogen is from 4 to 6.85 per cent. Oxygen and nitrogen are present in variable quantities from 7.59 to 36.1 per cent. The ash in good qualities is low, in earthy specimens is high, in many cases exceeding fifty per cent. Lignite does not yield coke. Aside from being utilized as fuel in the several localities where it is found, for both domestic and industrial purposes, it has been distilled for volatile constituents in Saxony.

*Peat, or Turf,* occurring in large areas in Ireland and in some parts of Europe, consists of the decayed remains of certain forms of plants. It has been, according to Mills, destructively distilled for tarry products, the industry, however, being no longer profitable.

The following tables, taken from the Reports of the Second Geological Survey of Pennsylvania, show the analyses of some of the more important varieties of American gas coals, coking coals, and non-coking, or block coals.

*I. Gas Coals.*

| | WESTMORELAND COAL COMPANY. | | | PENNSYLVANIA GAS COAL COMPANY. | | |
|---|---|---|---|---|---|---|
| | South Side Mine. | Foster Mine. | Larrimer, No. 2. | Irwin, No. 1. | Irwin, No. 2. | Sewickley. |
| Water at 225° . . | 1.410 | 1.310 | 1.560 | 1.780 | 1.280 | 1.490 |
| Volatile matter . | 37.655 | 37.100 | 39.185 | 35.360 | 38.105 | 37.153 |
| Fixed carbon. . | 54.439 | 55.004 | 54.352 | 59.290 | 54.383 | 58.193 |
| Sulphur . . . . | 0.636 | 0.636 | 0.643 | 0.680 | 0.792 | 0.658 |
| Ash . . . . . . . | 5.860 | 5.950 | 4.260 | 2.890 | 5.440 | 2.506 |
| Total . . . . | 100.000 | 100.000 | 100.000 | 100.000 | 100.000 | 100.000 |
| Coke, per cent. . | 60.935 | 61.590 | 59.255 | 62.860 | 60.615 | 61.357 |
| Fuel ratio . . . | 1 : 1.47 | 1 : 1.48 | 1 : 1.38 | 1 : 1.67 | 1 : 1.42 | 1 : 1.56 |
| | McCreath. | McCreath. | McCreath. | McCreath. | McCreath. | McCreath. |

## *II. Coking Coals.*

| | Connellsville, Frick & Co. | Bennington, Cambria Iron Company. | Broad Top, Barnet. | Broad Top, Kelley. | Cumberland. | Huntingdon County, Alloway Colliery. |
|---|---|---|---|---|---|---|
| Moisture . . . . | 1.260 | 1.400 | . . . | . . . | 1.10 | 0.250 |
| Volatile matter . | 30.107 | 27.225 | 16.00 | 19.68 | 15.30 | 14.510 |
| Fixed carbon . | 59.616 | 61.848 | 74.65 | 71.12 | 73.28 | 77.042 |
| Sulphur . . . . | 0.784 | 2.602 | 1.85 | 1.70 | 1.23 | 1.338 |
| Ash . . . . . . | 8.233 | 6.930 | 7.50 | 7.50 | 9.08 | 6.860 |
| Total . . . . | 100.000 | 100.000 | 100.00 | 100.00 | 100.00 | 100.000 |
| Coke, per cent. . | 68.63 | 71.375 | 81.00 | 71.00 | 83.59 | 85.24 |
| Fuel ratio . . . | 1:1.98 | 1:2.27 | . . . | . | 1:4.78 | 1:5.30 |
| | McCreath. | McCreath. | T. T. Morrell. | T. T. Morrell. | McCreath. | McCreath. |

## *III. Non-coking Coals (Block Coal).*

| | Mercer County, Pa., Sharon Coal. | Youngstown, Ohio. | Mercer County, Pa. | Straitsville, Ohio. | Brazil, Ind. |
|---|---|---|---|---|---|
| Moisture . . . . | 3.79 | 3.60 | 3.80 | . . . | . . . |
| Volatile matter . . | 35.30 | 32.58 | 25.49 | 36.50 | 40.15 |
| Fixed carbon . . | 53.875 | 62.66 | 68.03 | 55.60 | 57.20 |
| Sulphur . . . . . | 0.675 | (0.85) | 1.04 | 0.96 | 0.75 |
| Ash . . . . . . | 6.36 | 1.16 | 1.70 | 6.94 | 1.90 |
| Total . . . . | 100.000 | 100.00 | 100.06 | 100.00 | 100.00 |
| Coke, per cent. . . | 60.91 | . . | . . . | 61.00 | 58.00 |
| | McCreath. | Wormley. | Jno. Fulton. | Wormley. | Prof. Cox. |

*Effects of High or Low Temperature in the Distillation of Coal.*—Coal when distilled at a low temperature yields products of a very different nature from those obtained if the temperature employed had been high. On this subject Professor Edmund T. Mills, of Glasgow, in his little manual on "Destructive Distillation" (3d ed., p. 9), states that "at a very high temperature the products from coal and shales are carbon and carbonized gases of low illuminating power, with but little liquid distillate; at a low temperature there is much liquid product and gas of high illuminating power. The greatest amount of liquid product of low boiling-point is found in American and Russian petroleums, which have probably been produced by the long-continued application of a very gentle natural heat.

"When coal is slowly heated (as must be to a great extent the case when it is broken fine, or when a large retort is used), its oxygen is chiefly converted into water; when rapidly heated, the oxygen is expelled as carbonic oxides."

To show the verification of these principles in practice, the results of high and low temperature distillation upon three different coals may be quoted from the same authority:

*Yield of Gas, Oil, etc., from Shales and Coals at High and Low Heats.*

| | Good Shales. | | Boghead Coal. | | Gas Coal. | |
|---|---|---|---|---|---|---|
| | High heats. | Low heats. | High heats. | Low heats. | High heats. | Low heats. |
| Volatile matter. Gas | 13.65 | 2.54 | 37.32 | 4.83 | 20.49 | 6.49 |
| Ammonia-water | 3.65 | 6.47 | 2.43 | 3.23 | 3.09 | 7.24 |
| Tar or oil | 11.04 | 17.65 | 20.65 | 50.29 | 17.08 | 26.45 |
| Sulphur | 0.99 | ... | 0.18 | ... | 0.29 | ... |
| Water at 212° | 2.82 | .. | 0.80 | ... | 4.15 | ... |
| | 32.15 | 26.66 | 61.38 | 58.35 | 45.10 | 40.18 |
| Coke Fixed carbon | 4.16 | 10.81 | 9.01 | 12.40 | 45.00 | 49.93 |
| Sulphur | 1.05 | ... | 0.06 | ... | 0.34 | ... |
| Ash | 62.64 | 62.53 | 29.55 | 29.25 | 9.56 | 9.89 |
| | 67.85 | 73.34 | 38.62 | 41.65 | 54.90 | 59.82 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Coke (dry) per ton of shale or coal | 1,520 lbs. | 1,642.2 lbs. | 865 lbs. | 934 lbs. | 1,230 lbs. | 1,340 lbs. |
| Specific gravity of shale or coal | 1.818 | | 1.224 | | 1.296 | |

**Note.—The low heat results were gotten by distilling the sample in a two-inch iron tube in a gas-furnace.**

Lunge (Coal-Tar and Ammonia, 2d ed., p. 17) states that "The quantity, and to a much greater extent the quality, of the tar are influenced by the *temperature* at which the decomposition of the case is carried on. Low temperatures, with nine thousand cubic feet of gas per ton of coal, will yield, with some coals, sixteen gallons of tar; whilst at high temperatures the yield will be but nine gallons, with about eleven thousand cubic feet of gas, from the same coal."* If the temperature being a comparatively low one, mostly such hydrocarbons are formed as belong to a paraffin (methane) series, having the general formula $C_nH_{2n+2}$, along with the olefins, $C_nH_{2n}$. The lower members of this series are liquid, and, furnished in the pure state, are lighting and lubricating oils; the higher ones are solid and form commercial paraffine. They are always accompanied by oxygenized derivatives of the benzene series (phenols); but of these the more complicated ones predominate, in some of which methyl occurs in the benzene nucleus, in others replacing the hydrogen of hydroxyl,—*e.g.*, cresol, $C_6H_4(CH_3)(OH)$; guaiacol, $C_6H_4(OH)(OCH_3)$; creosol, $C_6H_3(CH_3)(OH)(OCH_3)$, etc. Liquid products prevail; and among the watery ones acetic acid (which is again a compound of the fatty series) is paramount. Of course also permanent gases are always given off, though in comparatively small quantity.

If, on the other hand, the coal has been decomposed at a very high temperature, the molecules are grouped quite differently. Whilst the olefins and members of the acetylene series still occur more or less, the hydrocarbons of the paraffin series disappear almost entirely; and from them are formed on the one hand compounds much richer in carbon, on the other hand more hydrogenized bodies. The latter always occur in the gaseous state; hence the gas so produced contains methane, or marsh-gas, $CH_4$, and free from hydrogen as principal constituents, and is very much increased in quantity. The carbon thus set free is partly deposited in the retorts themselves, and then occurs in a very compact graphitoidal form; another

* Davis, Journ. Soc. Chem. Ind., 1886, p. 5.

portion of the free carbon occurs in a state of extremely fine division in the tar, and forms a constituent of the pitch or coke remaining behind from tar-distilling; another portion contributes to the formation of compounds richer in carbon, belonging to the "aromatic" series, all of which are derived from benzene, $C_6H_6$. At the same time the action of heat effects further molecular "condensations," usually with separation of hydrogen, by which process compounds of a higher molecular weight are formed, as naphthalene, anthracene, phenanthrene, chrysene, etc. The never absent oxygen must also in this case cause the formation of phenols; but here phenol proper, or carbolic acid, $C_6H_5(OH)$, predominates, whilst cresol and the other homologues are diminished in quantity, and the dioxy-benzenes, as well as their methylated derivatives, disappear altogether. The above will be better illustrated by the statement (from Stohmann-Kerl's "Chemie," 3d ed., vi. p. 1162) that Zwickau glance coal yielded the following quite different products, according to whether it was put into a cold retort and gradually brought to a red heat (*a*), or distilled quickly from a very hot retort (*b*):

| | *a.* | *b.* |
|---|---|---|
| Coke | 60.0 | 50.0 |
| Water | 10.7 | 7.7 |
| Tar | 12.0 | 10.0 |
| Gas and loss | 17.1 | 32.1 |

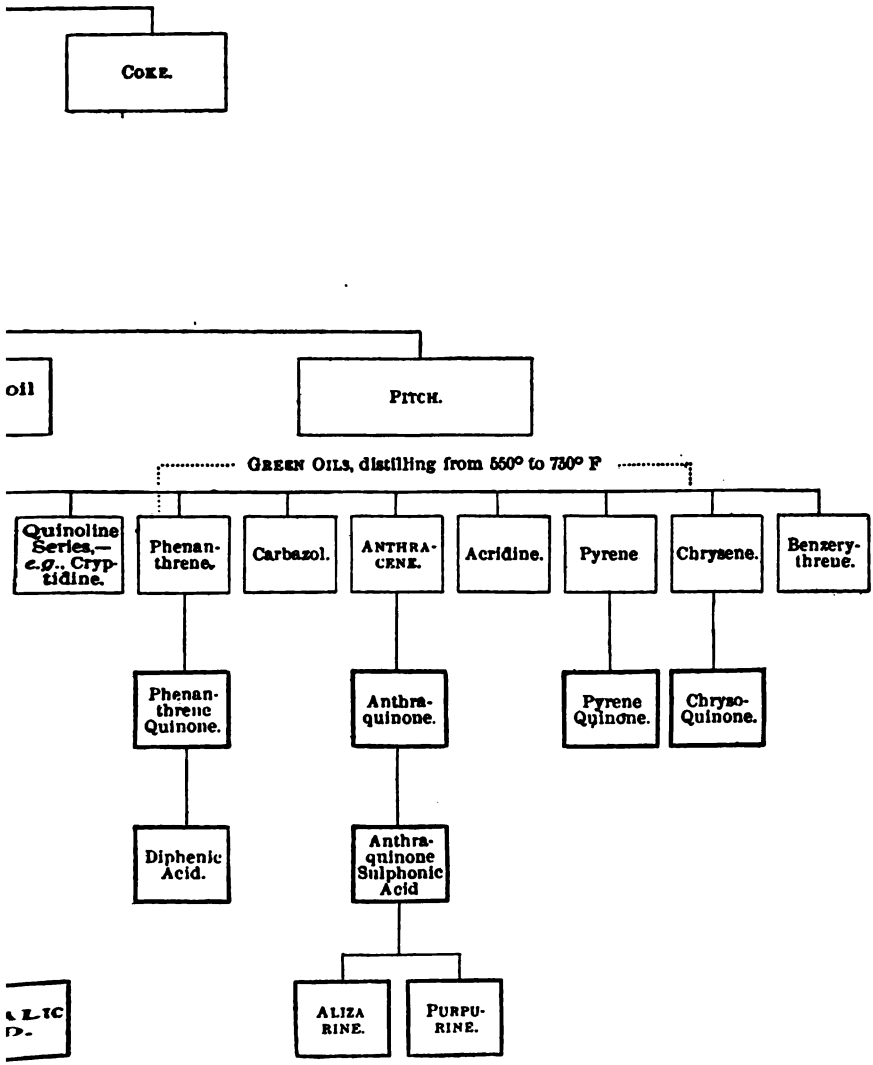
The tar from (*a*) consisted of photogen, paraffine oil, lubricating oil, paraffine, and creosote; that from (*b*), of benzene, toluene, naphthalene, anthracene (together with heavy oils corresponding to the paraffine and lubricating oil), and much creosote.

The annexed diagram, constructed by S. B. Boulton, and published in the Society of Chem. Ind. Journal, 1885, p. 471, represents the whole process of the destructive distillation of coal, including the subsequent treatment of the main fractions, and exhibits in their proper order the various products obtained therefrom.

## II. Processes of Treatment.

1. GAS-RETORT DISTILLATIONS OF COAL.—The distillation of coal as carried out in retorts differs from distillations of other substances mainly in the apparatus employed and in the nature of the substances to be recovered. For gas purposes, retorts, wherein the decomposition of the coal used takes place, are made use of, which were originally constructed of cast iron, about one inch in thickness, twelve to fifteen inches in width, and about seven feet in length, closed at the rear end, and provided at the front or mouth with a heavy shoulder or rim supplied with studs to which is attached a cast-iron extension, technically termed the "neck," which carries on its upper side a flange to which is secured upright pipes serving to lead the gases generated away from the retort. The front of the neck is provided with a screw-clamp to retain the lid or cap of the retort in position. Iron retorts are destroyed with great rapidity; the destruction being caused by the heat of combustion of the fuel used, the sulphur in the gas coal (an impurity always present in more or less quantity), which acts, forming sulphide of iron, and the carbon, which, as a carbide of iron, graphitic in appearance, forms layers within the retort from one to two inches in thickness. The oxygen of the air also has a very deleterious influence, especially upon retorts when heated redness.

oal when carbonized by the usual method for the

The direct products of the dead oils are arranged as nearly as possible according to their respective volatilities; and to the order in which they come over from the still.

oil

PITCH.

GREEN OILS, distilling from 550° to 750° F

Quinoline Series,—*e.g.*, Cryptidine.

Phenanthrene.

Carbazol.

ANTHRACENE.

Acridine.

Pyrene

Chrysene.

Benzerythrene.

Phenanthrene Quinone.

Anthraquinone.

Pyrene Quinone.

Chryso-Quinone.

Diphenic Acid.

Anthraquinone Sulphonic Acid

ALIZARINE.

PURPURINE.

LIC D.

In later years fire-clay retorts have been substituted for those made of cast iron, for the reason that they are more durable. These retorts are made of a mixture of clay and sand, and are furnished to the gas-works in several shapes, the semi-cylindrical being the one most generally employed. The sizes vary, six to nine feet in length, fifteen to twenty inches in width, and from ten to fifteen inches in height being the average, and take a charge of one hundred and fifty to two hundred pounds of coal. Retorts have been made up to nineteen feet in length, being charged from both ends.

The retorts, varying in number from five to seven, or even nine and more, are mounted in brick furnaces of special construction, in such a manner that the gases of combustion of the coal will pass around and over the retorts and out through a main flue leading to the chimney. The fuel employed can be either coal, coke, or a mixture of both. Gas as a means of firing has been used for the purpose, the method being based upon the well-known regenerative system of Sir William Siemens.

The retorts are charged by hand, care being taken to evenly distribute the coal over the *sole*, or bottom, and to close it quickly. Various attempts have been made to perform this laborious work with mechanical means, but at present no entirely satisfactory substitute has been found.

The products of distillation pass from the retorts proper through the neck, and upward through cast-iron *stand-pipes*, which are provided with *goose*-neck outlets, dipping below the surface of water in what is termed the *hydraulic main*.

It is in this part of the process that the main bulk of the tar is obtained, together with the ammonia-liquor. The hydraulic main is provided with an overflow-pipe through which all the tarry matters pass. This overflow-pipe leads to the tar-well, wherein the liquid products collect.

The gas having been freed from the tarry matters, etc., contained, passes from the hydraulic main with a considerably elevated temperature, carrying in a vaporized state hydrocarbons that would separate as its temperature is lowered. It is necessarily very important to remove these volatile and condensable products, which is effected by causing the gas to pass through a series of pipes, which reduces its temperature very close to that of the atmosphere. The older form of condenser was a series of pipes completely covered with water, similar to the worms as at present employed in connection with spirit and other distillations. This arrangement was replaced, however, by the forms now universally employed, and known as the atmospheric condensers, consisting of vertical pipes connected in pairs near the top by straight or curved pieces; the lower end of the upright pipes being connected to a box or trough containing water, divided by partitions, causing the gas to pass up and down alternately, as shown in Figs. 103 and 104. Tarry matters and more ammoniacal liquor are again obtained, which finds its way to the tar-well.

The gas after circulating through the condensers still contains impurities, which are removed by passing it through an apparatus known as the *scrubber*, consisting essentially of cylindrical wrought-iron towers filled with coke, over and through which trickles a light flow of water, or better, weak ammoniacal liquor; the gas passing upward, meets this downward flow of liquid, and to it gives up the hydrogen sulphide contained, with the formation of ammonium sulphide, etc. Tarry matters again are separated, and in time cause the coke to become somewhat clogged. This apparent drawback has led to the introduction of perforated iron plates in place of the

coke, or, what has also proved equally efficient, wooden lattice screens. Anderson's rotating scrubber consists of brushes, which while rotating dip into a trough of ammoniacal liquor, and thereby perform functions similar to the means above mentioned. Another form of scrubber consists of a tower containing cast-iron plates provided with perforations, through which ammoniacal liquor passes in its downward course, meeting the gas. The liquid is continuously pumped to the top, when it again passes down, coming in contact with fresh gas. This is repeated until the liquor has taken up sufficient ammonia to make it available to the ammonia sulphate manufacturer. From the scrubber the gas passes on to the *purifiers*, where the hydrogen sulphide still remaining, carbon-disulphide vapor, and the carbonic acid are removed. The purifiers ordinarily used consist of a large shallow box, constructed of cast iron in sections, and bolted together, or of wrought-iron plates, provided with a cover, the edge of which dips in water contained in a channel provided at the top of the box, acting as a seal and preventing the escape of gas at that point, as shown in Fig. 105. The purifying agent generally employed is slaked lime, which is spread upon wood screens, within the box, from four to six in number, one above the other, and supported by ledges. Hydrogen sulphide and carbon dioxide are absorbed by the lime, while compounds of cyanogen are at the same time decomposed.

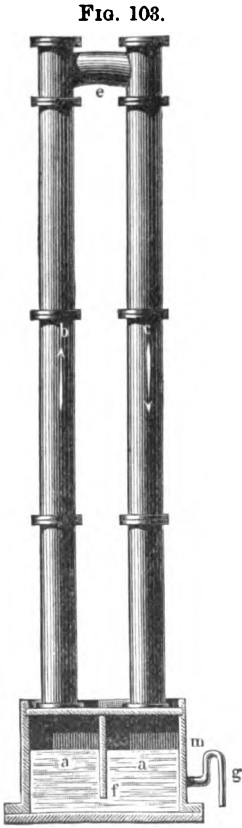
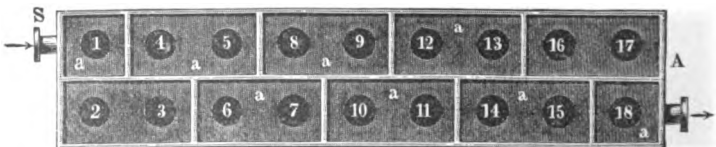



FIG. 103.

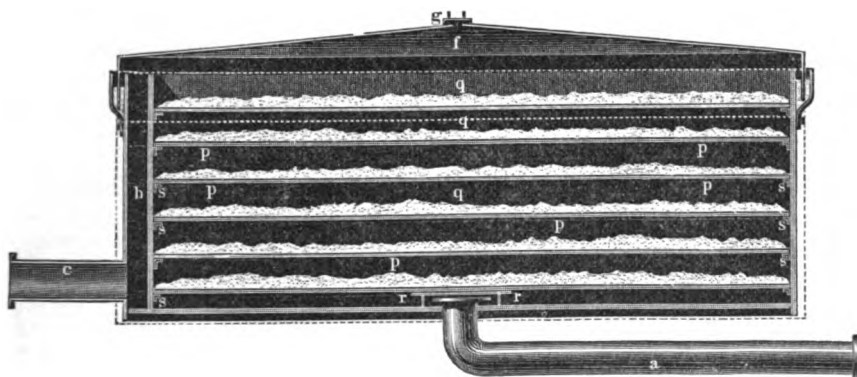
Four purifiers are generally used, three being in service, while the fourth is reserved charged with fresh lime. Gas enters the one containing the oldest lime, and when it is noticed that lead-acetate paper is discolored by some of the gas acting upon it, it is known that the purifying material is saturated; this purifier is discontinued, and the freshly-charged one placed in service. In this manner they are continually rotated.

Ferric hydrate (hydrated ferric oxide) is also largely employed in gas purification,—Laming process. Gas charged with hydrogen sulphide coming in contact with the above causes a reduction to ferrous sulphide, at the same

FIG. 104.

time some sulphur is deposited, with the formation of water. This process does not absorb the carbon dioxide from the gas; for this purpose lime is mixed with the ferric hydrate, together with some cinders or sawdust, in order that the whole may be porous, and resist as little as possible the passage of the gas. When the purifying action has ceased, simply exposing

the inert mixture to the action of the air for a while restores its properties, until after repeated use it becomes so charged with separated sulphur that it is no longer available.

The introduction of free oxygen into the gas, previous to it entering the purifiers, has been found to lengthen the time during which the oxide of iron can remain without being changed, thereby saving much handling. It

FIG. 105.

has also improved the illuminating power of the gas. (Journ. Soc. Chem. Ind., vol. viii. pp. 84 and 694.)

From the purifiers the gas passes through the meter of the works, where the volume is registered, then on to the gas-holders, where it is stored and from which it is distributed.

The following table illustrates the composition of illuminating gas taken from various stages of manufacture:

| | Entering the air-condenser. | Entering the scrubber. | Entering the Laming's purifier. | Entering the lime-purifier. | Entering the gas-holder. |
|---|---|---|---|---|---|
| Hydrogen | 37.97 | 37.97 | 37.97 | 37.97 | 37.97 |
| Marsh-gas | 39.78 | 38.81 | 38.48 | 40.29 | 39.37 |
| Carbonic oxide | 7.21 | 7.15 | 7.11 | 3.93 | 3.97 |
| Heavy hydrocarbons | 4 19 | 4.66 | 4.46 | 4.66 | 4.29 |
| Nitrogen | 4.81 | 4.99 | 6.89 | 7.86 | 9.99 |
| Oxygen | 0.31 | 0.47 | 0.15 | 0.48 | 0.61 |
| Carbon dioxide | 3.72 | 3.87 | 3.39 | 3.33 | 0.41 |
| Hydrogen sulphide | 1.06 | 1.47 | 0.56 | 0.36 | . . |
| Ammonia | 0.95 | 0.54 | . . | . . | . . |

2. COKE-OVEN DISTILLATION OF COAL.—The burning of coke in pits, "meilers," or mounds, represents the first rough and wasteful method of converting bituminous coal into coke; involving, at the same time, the total loss of all the volatile matter of the coal. It allows, however, of the smothering the finished coke with fine dust, instead of requiring it to be quenched with water, as in other methods. The so-called "bee-hive" ovens allow of the volatilizing of a much greater amount of sulphur in the coal, and give a decidedly increased yield of coke over the pit-burning method.

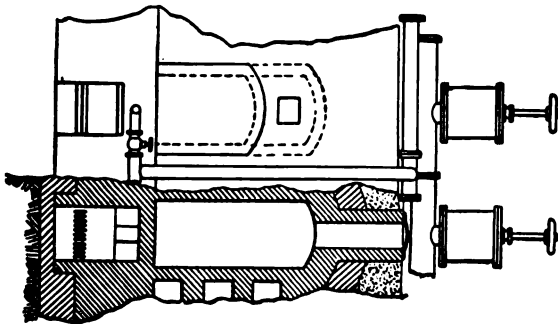
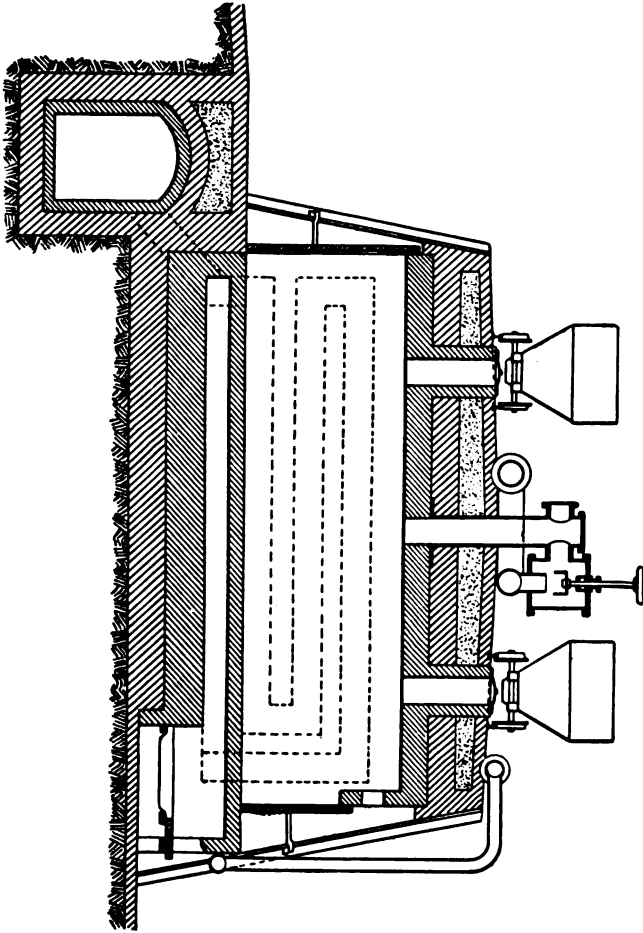
The charge can be run through, too, in less than half the time. Some air is admitted in both cases, with consequent loss of coke, and no attempt is made to save the residuals in either case.

The distillation of coal in ovens differs materially from the older methods of production in piles or kilns in that the inflammable gases given off are to some extent utilized.

*The Appolt's oven* consists of a series of vertical retorts built, generally, in two rows, enclosed by brick walls. Each retort is surrounded by air-spaces which are in communication one with the other, and with the inside of each retort. It is within this air-space that combustion of the gases generated by the decomposition of the coal occurs; air having been permitted to enter through openings for the purpose. The bottom of each retort is provided with a large door, which is opened to permit the charge of finished coke to fall into a pit built for the purpose.

*The Coppée's oven* is mainly employed in the coking of finely-divided coal. The shape of each chamber is long, slightly tapering, to facilitate the removal of the coke, narrow, and of a height equal to about three times the width. The gaseous products pass from the oven through vertical flues, built in the walls dividing the ovens, which open into horizontal flues under each chamber, thereby thoroughly distributing the heat. The waste gases are either led under steam-boilers, or are allowed to pass directly to the open air.

*The Simon-Carvés' oven*, illustrated in Fig. 106, is similar in construction to the Coppée oven, but provision is made for the recovery and utilization of the by-products. Mr. Henry Simon, C.E., in an address before the British Iron and Steel Institute (Journ. Iron and Steel Inst., No. 1, 1880), states: "According to our system, the coal is rapidly carbonized by subjecting a comparatively thin layer of it to a high temperature in a closed and retort-like vessel, and, whilst in the bee-hive ovens the volatile products are burned inside, we burn them around and outside of this retort-like vessel, and only after they are deprived of the tar and ammoniacal liquor. Each oven is in the form of a long, high, narrow chamber of brick-work, and a number of these are built side by side, with partition-walls between them sufficiently thick to contain horizontal flues. Flues are also formed under the floor of each oven, and at one end of these is a small fireplace, consisting of a fire-grate and ash-pit, with suitable door, the fire-door having fitted above it a nozzle, through which gas produced from the coking is admitted to form a flame over some fuel burning on the grate. Only a very trifling amount of such fuel, consisting exclusively of the small refuse coke, is used here, its function being really more that of igniting the gas than that of giving off heat. These grates are not charged with fuel more than twice in each twenty-four hours when in regular work. The products of combustion pass from the fireplace along a flue under the oven floor to the end farthest from the fire. They return along another flue under the floor to the fire end; they then ascend by a flue in the partition-wall to the uppermost of several horizontal flues formed therein, and *descend* in a zig-zag direction along these flues, finally passing into a horizontal channel leading to a chimney. The oven in consequence is evenly heated at the bottom and sides, and the coal contained is rapidly and completely coked. No air enters the chambers, the only openings being for the escape of the volatile products. The improved ovens are fed with coal by openings in the roof, over which coal-trucks are run on rails; and the coal is evenly

FIG. 106.

distributed by rakes introduced at end openings, provided with doors faced with refractory material, which doors are closed and kept tightly luted while the oven is in operation. The feed-holes in the roof are also provided with covers. Through the middle of the roof rises a gas-pipe provided with a hydraulic valve, which closes the passage by a lip projecting down from it into an annular cavity surrounding its seating, in which it is immersed in a quantity of tar and ammoniacal liquor, lodged there during previous distillations. The volatile products of the coal distillation rise by the gas-pipe, and are led through a range of pipes kept cool by external wetting, so that the tar and ammoniacal liquor become condensed and separated from the combustible gas." When the charge of coal has been converted to coke, it is removed from the ovens by means of a piston worked by an engine traversing rails in front of the battery. The yield of coke has been stated to be from seventy-five to seventy-seven per cent. of the coal. During a run of two hundred and fifteen days, the yield of residuals averaged 27.70 gallons of ammoniacal liquors per ton of coal carbonized, and 6.12 gallons of tar per ton of coal carbonized.

The yield of residuals in the Coppée-Otto oven has been found to average 25.44 pounds of sulphate of ammonia and 60.84 pounds of tar per ton of coal used.

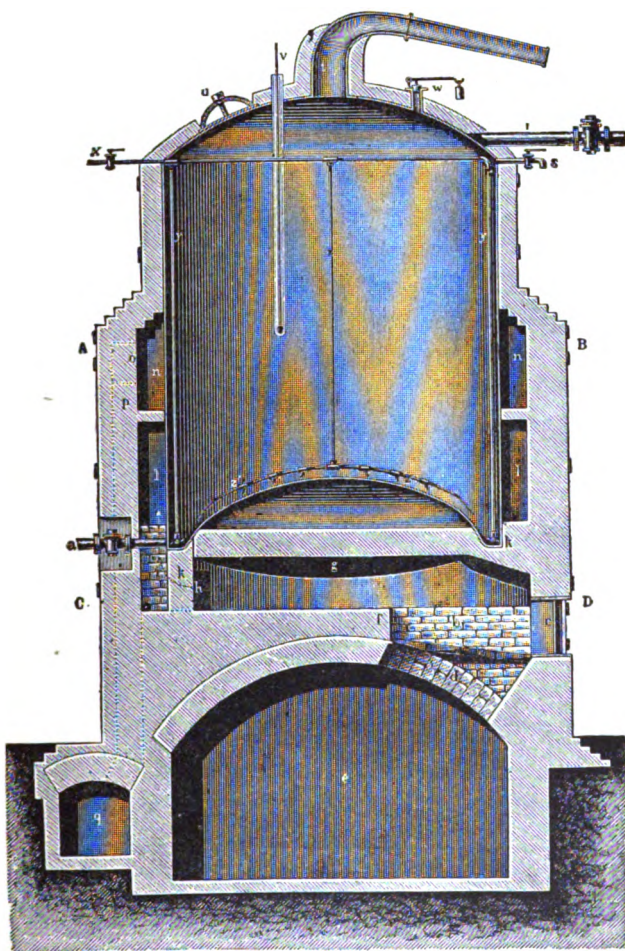
*The Jameson oven*, structurally considered, is but a simple modification of the common bee-hive oven, and is made by introducing channels in the floor of the oven radiating from the centre. These channels are covered with perforated tiles, and are, from the centre of the oven (where the channels are lowest), connected by means of pipes which lead to an exhausting apparatus, and also for the discharge of the products of distillation. In this process the products are removed as soon as they are formed, being drawn down by means of the suction applied through the mass of cooler coal than that from which they were generated.

Considerable difference exists between the tars obtained from the Simon-Carvé's and the Jameson coking processes. The first-mentioned tar has a specific gravity of 1.106, and closely resembles, chemically, the tars produced in the illuminating (retort) gas process, both being obtained at a high temperature. The Simon-Carvé's tar is rich in naphthalene and anthracene, but low in naphtha, benzene, phenols, etc. The Jameson tar is a low temperature tar, with a specific gravity varying from .960 to .994, and containing no benzene, but trifling amounts of toluene and xylene, while a considerable proportion of phenoloid bodies are found, containing, at the most, a very small quantity of carbolic acid.*

3. Fractional Separation of Crude Coal-tar.—Following gas retort distillation, in point of technical importance is certainly the distillation of the coal-tar obtained from the former processes and the separation therefrom of certain constituents which have a wide application in several industries. The same general mechanical arrangement, though somewhat simplified, is employed, consisting of a still, a condenser, and a receiver. The still should be constructed entirely of wrought iron, and can be either horizontal or vertical. Horizontal stills are, according to Lunge, far less economical than the vertical. Fig. 107 is a vertical section of a tar-still showing the construction and fittings. The heat from the fire on the grate *b*

* Consult Journ. Soc. Chem. Ind., 1883, p. 495, for tables of analyses of Simon-Carvé's and Jameson tars.

is prevented from impinging against the concave bottom of the still by means of the arch *g*, but passes through the openings *h* in the circular wall *k* into vertical flues *i*, from which it enters the annular space *l* and through flues in the front of the still to the upper space *n*, finally entering the flue *p*, which leads to the chimney. The supply-pipe *r* is for feeding the still, the pipe *s* is an overflow, and serves to indicate when the tank is full. The cock *a* is for drawing off the pitch. The still-head *t* is for conducting the vapors, and

FIG. 107.

is connected with the condenser. The system of pipes *x y z* indicated is for conducting superheated steam into the still for finishing the distillation; the pipes conforming to the shape of the bottom, are provided with a number of jets for a more equal distribution of the steam. The remaining attachments require no further mention.

The *condenser* consists of a coil of pipe immersed in water contained in an iron tank. In England, the pipe used is from six to nine feet in length,

and from four to six inches in diameter; the total length for one still is calculated at from one hundred and forty to two hundred feet. In Germany, preference is given to worms of iron (or lead, in which case the pipe from the still must be continued below the surface of the water in the condenser and join the worm there, in order to obviate the possibility of it being melted), made of two-inch pipe, and mounted in circular tanks provided with a steam-pipe for heating the water, and also with a small pipe connected with the worm for blowing in steam whenever it is necessary to clean it.

Connected with the condenser, and located at a safe distance from the still, is the *receiver*, which can be of any convenient shape, and of such a size as to contain the whole of one fraction; or a number can be employed, each acting as a store-tank and receiver. For the receivers to contain the volatile fractions, tight-closing covers must be supplied to guard against evaporation and fire, and the one containing the first fraction to have means for separating the oily from the watery layer. The receivers for the oils which deposit crystalline matter to be so arranged that they can be easily cleaned.

"Coal-tar (Allen, Commercial Organic Analysis, 3d ed., vol. ii., Part ii. p. 47), as obtained as a by-product in the manufacture of illuminating gas, is a black viscid fluid of a characteristic and disagreeable odor. The specific gravity ranges from 1.10 to 1.20, being usually between 1.12 and 1.15.

"As coal-tar is always more or less mixed with ammoniacal liquor, the constituents of the latter liquid are present in addition to those of the tar proper, and the constituents of the illuminating gas itself are also present in a state of solution.

"The first treatment of coal-tar on a large scale consists in distilling it in iron retorts and collecting the distillate in three or four fractions. The temperatures at which the receivers are changed vary considerably with the practice of different works, and hence the products are far from being strictly parallel."

The annexed table indicates the three most important methods of fractionation:

| A. | | B. | | C. | |
|---|---|---|---|---|---|
| Product. | Distilling-point ° C. | Product. | Distilling-point ° C. | Product. | Distilling-point ° C. |
| Crude naphtha, or light oils . | 0 to 170 | First runnings, or first light oils . . . . | 0 to 110 | Light naphtha | 0 to 110 |
| Heavy oils, dead oils, or creosote oils . . . | 170 to 270 | Second light oils | 110 to 210 | Light oils. . . | 110 to 170 |
| Anthracene oils . | above 270 | Carbolic oils . | 210 to 240 | Carbolic oils . | 170 to 225 |
| Pitch . . . . . | . . . . . | Creosote oils . | 240 to 270 | Creosote oils . | 225 to 270 |
| | | Anthracene oils | above 270 | Anthracene oils | 270 to 360 |
| | | Pitch . . . . | . . . . . | Pitch . . . . | . . . . . |

The principal constituents of coal-tar are separated, one from the other, by means of fractional distillation, a process depending upon the fact that, if a mixture of liquids, each having a different boiling-point, be heated, the one having the lowest will pass over first, and if the temperature is not

increased beyond that point at which the distillation of this fraction takes place, no other constituent will come over; if the temperature be gradually increased the others will follow in the order of their boiling-points. In cases where the boiling-points are close, and even in others where they are widely differing, the action of one substance upon another often prevents exact separations.

The hot stills (from the previous working) are charged with fresh tar, all the openings are then closed, and the fire carefully watched in order that no undue rise in temperature, and consequent boiling over of the contents, may take place. Gases, ammonia-liquor, and light oils distil over at 170°, the whole being designated "first runnings." This fraction is collected and allowed to stand, when the watery portion separates more or less completely from the oils, which are redistilled, yielding *ammonia* boiling under 70°, *crude benzol* at 140°, which is subsequently purified with sulphuric acid and distilled, *naphtha*, 140° to 170°, treated as the benzol, yielding "solvent naphtha." This whole fraction has a specific gravity nearly equal to that of water. The second fraction—"middle oil," or "carbolic oil"—distils over from 170° to 230°, and contains the impure phenols or carbolic acid and naphthalene. It is crystallized and pressed; the mother-liquor is agitated with caustic soda in an iron tank, the alkaline liquor (carbolate of soda) decomposed with sulphuric acid separating crude carbolic acid, which is distilled and crystallized, yielding liquid and pure carbolic acid in crystals. The unchanged oil from the soda treatment is returned to the second fraction for re-working. The press-cake from the first treatment of this fraction is purified with sulphuric acid, distilled, and yields naphthalene. The *third fraction* constitutes the *heavy* or *dead oil*, so called from the fact that the specific gravity is greater than water, and boils from 230° to 270°, occupying a position between middle oil and the anthracene fraction. It is subjected to no further treatment, but is employed chiefly for preserving timber, varnish manufacture, burning for lamp-black, etc. The fourth fraction, or *anthracene oil*, boiling over 270°, constitutes the green oil or green grease, from which, upon subsequent treatment, the commercial anthracene is obtained. This fraction is allowed to stand for some time, in order to cool and to separate the crystallizable substances, when the mass is drained from the excess of oil and pressed. The press-cake is crude anthracene, which is dissolved in naphtha and known as *fifty per cent. anthracene.* The mother-liquor from the first pressing with the drainings are redistilled, crystallized and pressed, yielding crude anthracene, treated as above, and anthracene oil. The residue in the still constitutes *pitch*, which is withdrawn and employed for making pavements, varnishes, etc.

The annexed diagram from Ost's "Lehrbuch der Technischen Chemie" graphically represents the preceding outline of the tar distillation process.

4. TREATMENT OF AMMONIACAL LIQUOR.—The ammoniacal liquor of the gas-works is that which passes out continuously from the scrubbers and other parts of the process, and is the chief source of nearly all the ammonia of commerce. According to Lunge, ordinary gas-liquor contains the following:

(*a*) *Volatile at ordinary temperatures.*

Ammonium carbonates (mono-, sesqui-, and bi-).
Ammonium sulphide $(NH_4)_2S$.
Ammonium hydrosulphide, $NH_4.HS$.

COAL-TAR,
Free from water, distilled.
AMMONIA-LIQUOR and first light oils boiling at 170°. Distil.
MIDDLE OIL, boiling from 170° to 230°. Crystallize and press.
HEAVY OIL, boiling from 230° to 270°.
ANTHRACENE OIL, boiling over 270°. Crystallized and pressed.
PITCH.
AMMONIA under 70°.
CRUDE BENZOL boiling at 140°, purified with sulphuric acid and distilled.
NAPHTHA boiling at 140° to 170°, purified with sulphuric acid and distilled.
Residue boiling over 170°.
Mother-liquor, agitate with caustic soda.
SOLID CRUDE NAPHTHALENE, purified with sulphuric acid, distilled or sublimed.
CRUDE ANTHRACENE.
ANTHRACENE OIL, again distilled and crystallized.
Acidulate the caustic soda solution with sulphuric acid to separate crude carbolic acid. Distil and crystallize.
Insoluble in caustic soda returned to the middle oil.
CRUDE ANTHRACENE.
OIL.
Mixed with Naphtha.
PURE CARBOLIC ACID in crystals.
LIQUID CARBOLIC ACID.
CRUDE BENZOL of fifty per cent. or ninety per cent., boiling from 70° to 140°. Is used in the aniline-color works.
PURE NAPHTHALENE.
CRUDE ANTHRACENE of fifty per cent.
AMMONIA under 70°.
CRUDE BENZOL of fifty per cent. or ninety per cent.
SOLVENT NAPHTHA.
PURE CARBOLIC ACID. Crystals.
LIQUID CARBOLIC ACID.
NAPHTHALENE.
HEAVY OIL.
CRUDE ANTHRACENE of fifty per cent.
ANTHRACENE OIL.
PITCH.

Ammonium cyanide.
Ammonium acetate (?).
Free ammonia.

(*b*) *Fixed at ordinary temperatures.*
Ammonium sulphate.
Ammonium sulphite.
Ammonium thiosulphate (hyposulphite).
Ammonium thiocarbonate.
Ammonium chloride.
Ammonium thiocyanate (sulphocyanide).
Ammonium ferrocyanide.

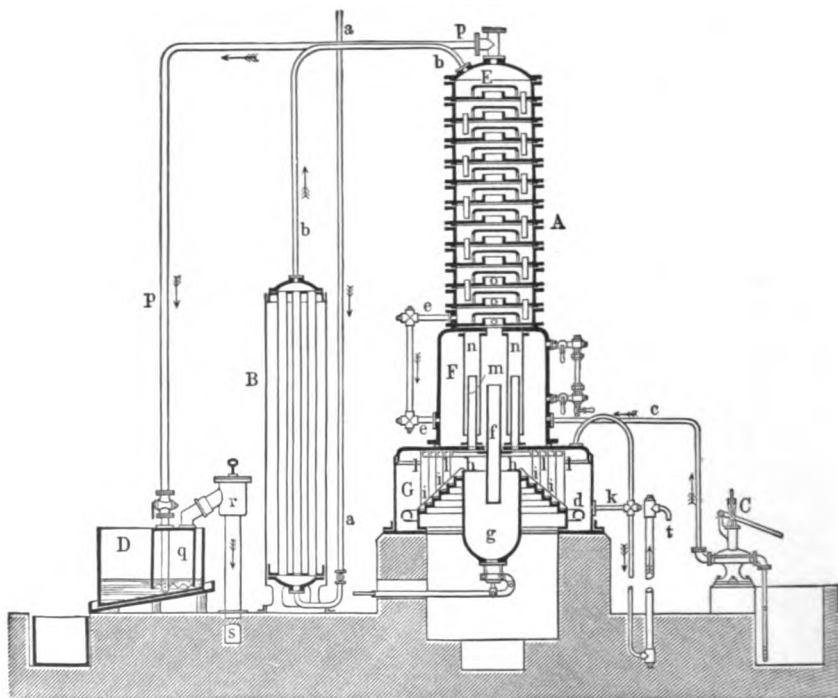
The salts of ammonia that are volatile are readily removed from the gas-liquor upon simply boiling, or by the aid of steam. The fixed ammonia salts require the addition of chemical agents—*e.g.*, lime—to break up the combination and liberate the ammonia which is eventually recovered. The greater the amount of volatile ammonia and less the amount of the non-volatile compounds, the greater the value the liquor has for treatment.

The method of recovering ammonia at a London works, where one hundred thousand gallons of liquor are treated daily, is briefly outlined as follows: The liquor is pumped into a large settling-tank, where, after remaining for a day or more, it is pumped into a "Coffey" still, thirty feet high, into which steam at two atmospheres pressure is blown. By this treatment the volatile ammonium compounds are separated from the water and the non-volatile compounds. Carried along with the steam, the volatile compounds pass from the still through a worm, provided with half-inch holes, into a sheet-lead saturator filled two-thirds with 140° Twaddle sulphuric acid and water. This water so dilutes the acid that it prevents the ammonium sulphate from crystallizing within the saturator. After saturation, steam is blown through the solution to remove hydrogen sulphide, which, after passing through a condenser, is burned; the heat generated being partly utilized in the production of steam for the operation. The saturated liquid is run off into leaden pans placed over a fire, and evaporated to such a point that the sulphate will crystallize out. The residual mother-liquor is made use of in the dilution of the sulphuric acid in the saturator.

Without going into the details of construction of the many improvements made in the apparatus employed for the recovery of ammonia, it may be well to mention the apparatus of Grüneberg and Blum, Fig. 108. *A* is the column, *B* the economizer through which the gas-liquor passes before entering the still, and is heated by means of steam or waste gases. *C* is the pump which introduces the lime into the lime-vessel *F*. *D* is the acid-tank or saturator. The gas-liquor enters the still at the top and descends from chamber to chamber, meeting the upward current of steam, till it reaches the lime-decomposition-tank *F*, and finally the boiler *G*. In this is a peculiar truncated cone, *l*, over which flows the liquor from step to step, and owing to the increased area of each step the liquor becomes thinner and thinner, permitting the steam to act very thoroughly. The ammonia generated passes from the still through the pipe *P* to the saturator *D*. Waste gases collect in the bell *q*, from which they are led to the economizer *B*, and finally burned.

*Feldmann's apparatus* is a steam still, capable of recovering both the volatile and fixed ammonia, and occupies very little space. It consists of a chambered column, lime-tank, and an auxiliary column, in connection with

feed-tanks, economizer, lime-pump, and saturator. The liquor flows from the feed-tanks through the economizer, where it is heated, to the top of the main column, down which it flows successively through the chambers in which it is boiled into the decomposing-tank, which contains lime, where it is thoroughly agitated with steam. The liquor flows from this tank to the auxiliary column, similar to the first one, where the little ammonia found is driven out. The spent liquor collects in the lower compartment, from which it constantly flows away. Lunge states that an apparatus to distil from

Fig. 108.

eight to ten tons of ammoniacal liquor daily occupies a space of seventeen feet by thirteen feet by ten feet.

The sulphate of ammonia as it is fished from the saturators is allowed to drain, sometimes slightly washed with water, and sold without drying.

## III. Products.

Under this head will be considered the more important products that are obtained by the subsequent treatment of the main fractions of the distillation process as indicated on previous pages.

1. First Light Oil is the fraction distilling at a temperature up to 170° C. It includes a small percentage of ammonia-liquor which is mechanically contained in the tar, and is separated from the tar oils by being allowed to stand and settle out when it is drawn off. The specific gravity of the fraction is about .975, and is made up of benzene, toluene, and higher homologues, with phenol, cresol, naphthalene, etc. The products obtained from it are separated by redistilling the whole fraction in a small still of

the same general type as the large tar-still. The separate distillates are generally as follows:

*First Light Oil up to 170° yields*

(*a*) To 110° . . . . . . . . . . . . . . . . . . . . " 90 per cent. benzol."
(*b*) 110° to 140° . . . . . . . . . . . . . . . . . . . " 50 per cent. benzol."
(*c*) 140° to 170° . . . . . . . . . . . . . . . . . . . solvent naphtha.

The fraction obtained up to 110° is chemically washed, being agitated with sulphuric acid of 1.84 specific gravity in the proportion of one pound to one gallon of oil, which combines with the bases, dissolves resins, etc. The agitation is carried out in cast-iron or lead-lined wooden tanks securely covered to prevent loss of the volatile bodies, and provided with mechanical means for mixing. This is completed in ten or fifteen minutes, when the whole is allowed to stand at rest for an hour or more, and then the spent acid is completely removed. The oil is now thoroughly washed four or five times with water, until no color is imparted to the washings, which should have but a slight acid reaction. Agitation is again continued, but with a ten per cent. caustic soda solution, afterwards allowed to separate, when the alkaline solution is removed, when the oil is finally washed with water and distilled, either by means of fire or steam.

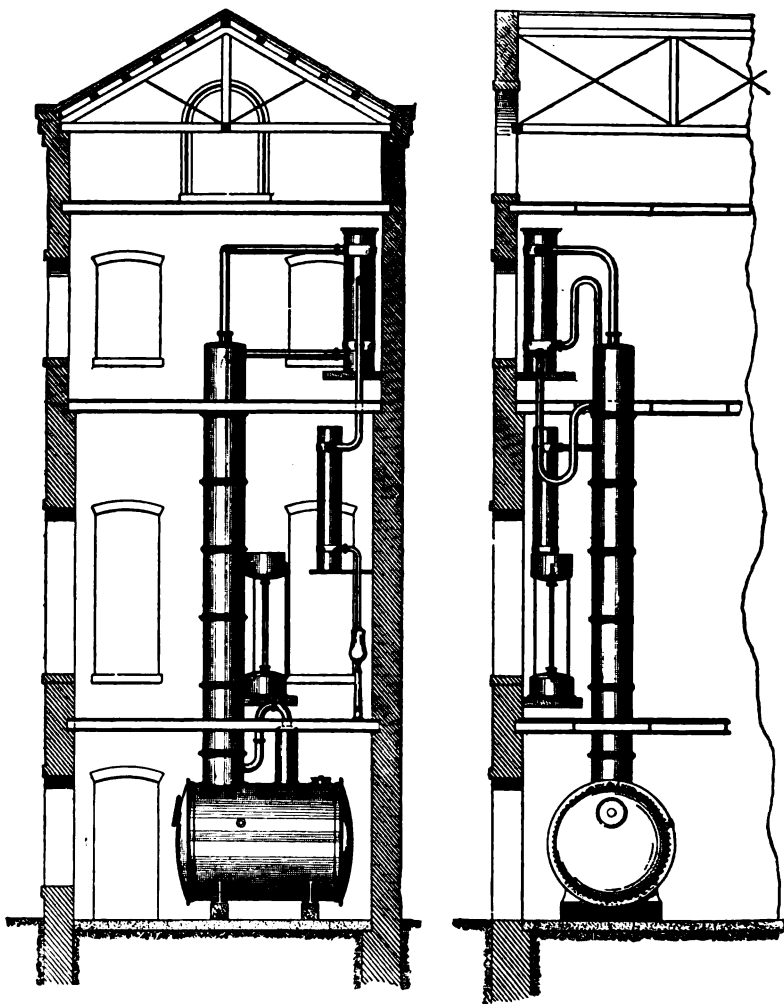
(*a*) "*Ninety per Cent. Benzol.*"—The product coming over at 110° is designated " ninety per cent. benzol," from the fact that ninety per cent. by volume of it distils before the thermometer rises above 100° C. A. H. Allen (Commercial Organic Analysis, 2d ed., p. 489) states: " A good sample should not begin to distil under 80° C., and should not yield more than twenty to thirty per cent. at 85°, or much more than ninety per cent. at 100°. It should wholly distil below 120°. . . . The actual percentage composition of a ninety per cent. benzol of good quality is about seventy per cent. benzene, twenty-four per cent. toluene, including a little xylene, and four to six per cent. of bisulphide of carbon and light hydrocarbons. The proportion of real benzene may fall as low as sixty or rise as high as seventy per cent. Ninety per cent. benzol should be free from opalescence and colorless (' water white'). The specific gravity is between .88 and .888 at 15.5° C. (= 60° F.), but this is not a true guide as to the quality, from the fact that bisulphide of carbon (specific gravity 1.27) and light hydrocarbons (specific gravity .86) sensibly affect the specific gravity of the benzol."

(*b*) "*Fifty per Cent. Benzol*" is a product of the fraction boiling from 110° C. up to 140° C., and is subjected to the same treatment as the previous one. The specific gravity of this benzol varies from .867 to .872 in the Scotch, to .878 to .88 in the English, samples. Is nearly free from bisulphide of carbon, and contains little hydrocarbons, while the per cent. of toluene and xylene are greater than in the ninety per cent. benzol.

The benzols as such are not employed in the arts to a very great extent, but when *nitrated*, nitrobenzene (mirbane oil) is obtained, which is used as such for scenting soaps and pomades; and when this nitrobenzene is reduced by iron turnings, etc., *aniline oil* is produced, which enters largely into the manufacture of many of the artificial coloring matters.

(*c*) *Solvent Naphtha*—so called from the use to which it is put,—dissolving caoutchouc in the manufacture of water-proof materials, etc.,—follows the benzols, boiling over 140°, and consists of xylene, pseudocumene, and mesitylene. In some works the distillation of this fraction is not driven to the end, but stopped when the product yields ninety per cent. at 150°, the residue being distilled as *burning naphtha* with a specific gravity of .90.

Lunge states: "From the product distilled up to 140° may be extracted sixty or seventy per cent. of fifty per cent. benzol, twenty to twenty-five per cent. of carburetting and solvent naphtha, five to eight per cent. of burning naphtha. The product distilled between 140° and 170° yields twenty-five to fifty per cent. best naphtha, fifty to twenty-five per cent. burning naphtha, and twenty-five per cent. residue in the still." The

Fig. 109.

separation of the preceding into benzene, toluene, xylene, etc., for the use of the color manufacturer, is not ordinarily carried out in the tar-distillery, but at the color-works, in especially constructed column stills. The appearance of such a benzene rectification still is shown in Fig. 109. For details of construction of such a column still, see Chapter VI. p. 222.

The following table (Lunge, "Coal-Tar and Ammonia," 2d ed., p. 476) shows the yield in percentage volumes of the products from the light tar oils:

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| COMMERCIAL PRODUCTS. | Initial boiling points. | ° C. 88. | ° C. 93. | ° C. 100. | ° C. 110. | ° C. 120. | ° C. 130. | ° C. 138. | ° C. 149. | ° C. 160. | ° C. 171. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | ° C. | | | | | | | | | | |
| " Ninety per cent. benzol" | 82 | 30 | 65 | 90 | | | | | | | |
| " Fifty per cent. benzol" | 88 | . . | 13 | 54 | 74 | 90 | | | | | |
| Toluol . . . . . . . | 100 | . . | . . | . . | 56 | 90 | | | | | |
| Carburetting naphtha . . | 108 | . . | . . | . . | 1 | 35 | 71 | 84 | 97 | | |
| Solvent naphtha . . . . | 110 | . . | . . | . . | . . | 17 | 57 | 71 | 90 | | |
| Burning naphtha . . . . | 138 | . . | . . | . . | . . | . . | . . | . . | 30 | 71.5 | 89 |

2. MIDDLE OIL.—This constitutes the second main fraction in the tar distillation process, and is collected between 170° and 230° C., yielding upon further treatment two very important and valuable products: liquid and solid *carbolic acid* and *naphthalene*, both of which find their widest application in the artificial-color industry, although large quantities are employed for many other purposes.

While this fraction is coming over from the still, no cold water is allowed to run into the condensing-tank, for the reason that a reduction of temperature to the point at which solid naphthalene would form in the condenser is to be avoided; a steam-pipe is generally led into the tank, and the water brought to 50° or 60°, thereby keeping crystallizable matter in a fluid condition and continually flowing.

This distillate is allowed to become cold, when nearly all of the naphthalene separates in leaflets, which are drained and pressed to expel the remaining portions of the non-crystallizable oil, which is the source of the carbolic acid.

1. *Carbolic Acid.*—The above oils are thoroughly mixed with a solution of caustic soda (specific gravity 1.26) in a tank provided with mechanical agitators, or with means for forcing air through the liquids. The mixing is performed at a temperature of from 40° to 50°, and is completed in one to one and a half hours, when, after standing to allow the alkaline liquors to subside, they are drawn off and cautiously decomposed by adding sulphuric acid till the liquor has an acid reaction, when it is at once removed to avoid the crystals of sodium sulphate forming in the tank; the carbolic acid is allowed to stand for a few days in order that any sodium sulphate solution remaining may separate out, when it is washed with water and finally distilled in small retorts, yielding, in the first fraction, *water and oil;* in the second, *crystallizable oil*, from which is obtained the *crystal carbolic acid* of commerce; and in the third fraction, the *non-crystallizable phenols*, or *liquid carbolic acid.*

That part of the mother-liquor from the naphthalene which is not acted upon by the caustic soda solution added to remove the phenols is returned to the main middle-oil fraction and again re-worked.

*Carbolic Acid, or Phenol*, $C_6H_6O$ (or $C_6H_5OH$).—All compounds containing the group OH in place of one or more of the hydrogen atoms of benzene ($C_6H_6$) or its homologues, are designated *Phenols.* Carbolic acid has a very peculiar and characteristic odor, burning taste, is poisonous, and has preservative properties; the odor, however, is not so pronounced in pure as in impure specimens. The specific gravity at 0° is 1.084, crystallizes in colorless rhombic needles which melt at 41°, boiling at 182°, and is not decomposed upon distillation. At ordinary temperature it dissolves in

water with difficulty (1 : 15), but is soluble in alcohol, ether, glacial acetic acid, and glycerine in all proportions. Upon exposure to light and air it deliquesces, and acquires a pinkish color. The most extensive use made of it is as a raw material in the manufacture of many of the artificial coloring matters,—picric acid, used as a yellow dye, and which finds considerable application in the manufacture of a number of high explosives. Large quantities of various qualities of carbolic acid are consumed annually for antiseptic purposes, both for domestic use and in surgery.

2. *Naphthalene*—The crude crystals which were obtained when the middle-oil fraction was allowed to cool, and also from the treatment by distillation of the unchanged oil from the carbolic acid separation, are purified by fusing and mixing thoroughly with caustic alkali, if impure, followed by a washing with hot water, and afterwards with sulphuric acid; if the naphthalene operated upon is of a better quality, the alkaline treatment may be dispensed with, and the refining commenced with the acid, which is of 1.453 specific gravity; Lunge states, however, that this is too weak, and recommends an acid of 1.70 specific gravity, 1.84 specific gravity being still better. The amount of acid used varies from five to ten per cent.; the mixing being performed in lead-lined tanks, after which it is washed with water several times, and to remove the remaining traces of acid weak caustic liquor is used. The naphthalene thus purified is sublimed in barrels hung over melting-pots suitably mounted, or in frame or brick chambers connected by proper openings with an iron melting-pan, the general construction of which is shown in Fig. 110. The best naphthalene is produced by distillation from stills, which are made shallow, with a very high dome. Larger quantities are handled by this method than by subliming.

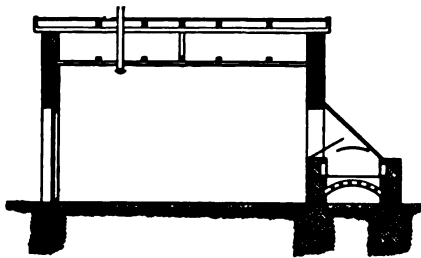



FIG. 110.

*Naphthalene*, $C_{10}H_8$, is one of the principal constituents of coal-tar, occurring in it in various proportions from five to ten per cent.; it is also formed when the vapors of organic substances are passed through tubes heated to redness. The specific gravity of naphthalene when solid is 1.158, at its melting point (79.2°) it is 0.978; it boils at 216.6° C. The odor is pleasant, though characteristic; volatilizes to some extent at ordinary temperature, but readily in the vapor of boiling water. Crystallizes in large, silvery-brilliant, thin rhombic plates, which are faintly soluble in hot, but insoluble in cold, water, though easily in methyl and ethyl alcohols, chloroform, ether, benzene, etc. The commercially sublimed naphthalene is from seventy to ninety-nine per cent. pure. Industrially, it is employed in the manufacture of a large series of coloring matters; as an enricher ("carburetter") of illuminating gas; and when specially refined, as a substitute for ordinary camphor in preventing the ravages of insects, etc., in woollen goods.

3. CREOSOTE OIL, OR HEAVY OIL, constitutes the third main fraction, and is generally collected from 230° to 270° C., or until it is noticed that solid matters begin to crystallize, which indicates that the *anthracene* is commencing to distil. In order to prevent any cresols from contaminating the phenol and naphthalene of the previous fraction, that fraction is not driven

to completeness, which precludes the possibility of any of the heavy oil passing over. Any naphthalene contained in this fraction is recovered by crystallizing and pressing, the residual oil not being subjected to further treatment is employed directly.

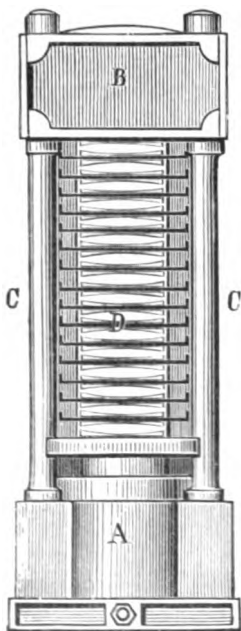
The oil has a greenish-yellow color, and is very fluorescent, which increases in intensity upon exposure to light and air. By transmitted light it is dark red, and by reflected light the appearance is bottle-green. The odor is unpleasant and extremely characteristic. It is heavier than water, the last portion coming from the still being as high in specific gravity as 1.10. Creosote oil has been found to contain naphthalene, anthracene, phenanthrene, phenol, cresol, etc., with many other bodies but little known. It finds its widest application in the *creosoting* or *preservation of timber;* although, to a limited extent, it has been employed as a fuel, and for the production of illuminating gas, softening hard pitch, as a lubricant, for lamp-black production, etc.

The process of impregnating timber with coal-tar oils, with the view of preserving it against decay, dates from 1838, when a patent was granted to John Bethell. This process consists essentially of exhausting the already seasoned timber of air and moisture in a vacuum maintained by means of an air-pump; when the exhaustion is complete, the tar oil is allowed to enter the vessel, when it is at once absorbed by the pores of the wood. Various processes have been suggested from time to time, but those which have given the most complete satisfaction are nearly all based upon the one above mentioned. S. B. Boulton's process is suited to the treatment of raw timber, and is similar in some respects to Bethell's; the vacuum is continued after the creosote oil (having been previously heated to 100° C.) has entered the vessel, the oil penetrating the pores of the wood very thoroughly.

4. ANTHRACENE OIL.—The fraction distilling from 270° C. and over consists of that portion of the tar which is made up of bodies possessing the highest boiling points, and is distinguished from the heavy oil fraction by a separation, on cooling, of solid matters. In it has been found *naphthalene, methyl-naphthalene, anthracene, phenanthrene, methyl-anthracene, pyrene, carbazol,* etc. With the exception of methyl-naphthalene, which is a liquid, all the others are solids at ordinary temperature, but which have high melting points.

The separation of the crude anthracene from the distillate is accomplished by cooling or crystallizing, and pressing. The cooling takes place in large, shallow iron pans, either spontaneously or by refrigeration, when the semi-solid mass is transferred to bag filters, closed at the lower end, and connected by means of nipples at the upper end to a pipe for conducting compressed air, which acts in driving the liquid or non-solidifying portion out, and leaving the mass nearly dry. By using filter-presses instead of the above, a larger and better yield can be obtained in a shorter time. The crude anthracene is placed in cloths and subjected to a gradually-increasing pressure in a vertical or horizontal hydraulic press, the plates of which being so constructed as to be heated by steam, or the whole press may be enclosed in a chest to which steam can be admitted. Fig. 111 illustrates the general arrangement of a press suited to the purpose. The use of heat in the pressing is to cause those bodies which have a lower melting point than that of the anthracene to be easily removed. The yield of anthracene by hot-pressing only comes up to about thirty to thirty-two per cent. of the oil in winter, and thirty-three to thirty-six per cent. in

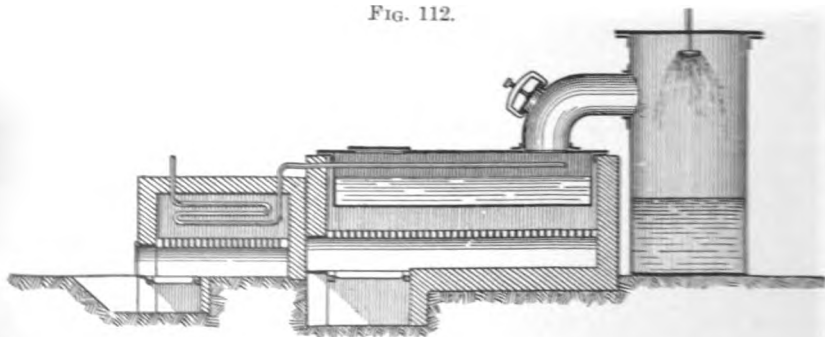
summer (Lunge). The pressed anthracene is ground to a fine powder, and washed with solvent naphtha (which removes the coal-tar oils) in either a horizontal or vertical air-tight boiler, fitted with a steam coil, and provided with a mechanical agitator. The mixing requires several hours with gentle heat, when the whole is forced by compressed air to a closed filter, which separates the now washed anthracene from the naphtha.

Fig. 111.

A still purer anthracene is obtained by submitting this product to sublimation with the aid of steam. For this purpose the apparatus shown in Fig. 112 is employed. The anthracene is melted in an iron pan, and over the surface of the melted mass superheated steam is blown. The anthracene vapors are carried by the steam into a cooling chamber, where they are condensed by coming in contact with a spray of cold water.

The anthracene oils from the first draining of crude material are usually re-distilled in order that the anthracene contained in them may be recovered. Graham's process (Chem. News, xxxiii. pp. 99, 168) for this is to distil about fifteen hundred gallons of the filtered oils from a clean tar-still until crystals of anthracene are noticed, when a sample of the distillate is allowed to cool, at which point the operation is stopped, and the residue in the still is run out and allowed to become cold, when the product separates out. This is filtered and pressed in the manner above described for the first crystallization.

The oils which yield no more anthracene when subjected to further treatment are added to the creosote oils, or else employed to soften pitch, etc.

Anthracene, $C_{14}H_{10}$, is found under similar conditions to those giving rise to naphthalene, and was discovered in 1832 by *Dumas* and *Laurent*, while *Fritzsche* was the first to find it in coal-tar, in which it occurs as a

Fig. 112.

characteristic constituent. When pure, it crystallizes in white, lustrous, rhombic plates, which exhibit a beautiful violet fluorescence. Melts from 210° to 213° C., subliming at about the same temperature in small scales. It is insoluble in water, sparingly in alcohol, while benzene, essential oils

light tar oils, and hot alcohol dissolve varying quantities. When oxidized it yields *anthraquinone*, which is further treated in the processes for the production of the valuable alizarine and other coal-tar colors, and which forms practically the only utilization for anthracene.

5. PITCH.—By *pitch* is understood the residue remaining in the still after nearly all the volatile constituents have been driven off. Formerly, what remained in the still after the light oils were distilled was called *asphalt*, and was equivalent to about eighty per cent. of the tar, consequently it contained those constituents mentioned in the middle oil and creosote oil fractions, with the anthracene. This method of fractionation, however, is not followed, but the distillation is generally carried to that point when the distillate shows a specific gravity of 1.09, when soft pitch will result. If the distillation is carried further, or until it has a specific gravity of 1.12, hard pitch is obtained. In some cases the distillation is pushed as far as the still will stand with safety, in which case no more volatile bodies remain and a coke virtually remains. As a rule, a moderately hard pitch is made, which is run into casks or barrels directly from the still.

The utilization of the pitch is carried out in several ways: in the manufacture of *patent fuel* (*briquettes*) when incorporated with coal-dust or coke-refuse. This industry has but little, if any, importance in the United States, but is quite extensive in Europe. Briquettes contain from five to eight per cent. of pitch, according to the amount of pressure employed in their manufacture. Good grades have ten per cent. more heating effect than ordinary steam coals, are more cleanly and economical.

The pitch mixed with creosote oil to the consistency of paint is much employed as such on iron- and wood-work where a black coating is desirable; various other substances are used as solvents and softeners, notably carbon bisulphide, which has given excellent results. In street-paving, the employment of the pitch has superseded the use of the natural asphalt to advantage. Considerable quantities are annually consumed in the manufacture of roofing-paper, etc.

## IV. Analytical Tests and Methods.

1. VALUATION OF TAR SAMPLES.—Practically, the most efficient method to follow for the determination of the value of tar samples is to distil twenty or thirty gallons from a small still, in the same manner and under, as far as possible, the same conditions as is practised in the distillation of tar on a large scale. The products are weighed and measured. When a small still is not accessible, recourse must be had, for laboratory purposes, to the following method, which gives excellent results if carefully attended:* "Two hundred and fifty cubic centimetres, or ten ounces measure, of the tar is placed in a retort which it only one-third fills, so as not to spoil the distillate if there is much frothing during distillation. The retort should be supported on a cup-shaped piece of coarse wire gauze, placed in an aperture in a sheet-iron plate. Over the retort is placed a dome, made by removing the bottom from a tin can or bottle, and cutting out a piece of the side to allow the neck of the retort to pass through. This contrivance confines the heat, and prevents the distillate or heavy vapor from falling back." . . . "The products obtained by the distillation are: (1) Ammoniacal liquor; (2) total light oils; (3) creosote oil; (4) an-

* A. H. Allen, Commercial Organic Analysis, 3d ed., vol. ii., Part ii. p. 52.

Upon the gradual addition of bromine to a solution of phenol a white turbidity (mono-brom-phenol, $C_6H_4BrOH$) is formed. If the solution is dilute no precipitate occurs, but upon the addition of more bromine, di-brom-phenol ($C_6H_3B_2OH$) is formed; upon further addition of bromine a very bulky precipitate is produced, which is separated as the insoluble and characteristic tri-brom-phenol ($C_6H_2Br_3OH$). This determination of phenol was first suggested by Landolt, though brought to perfection and used as a volumetric method by Koppeschaar (Z. a. Chemie, xvi. 233).

For the assay of carbolic acid the specific gravity is always noted, which ranges between 1.04 and 1.065; the lower figure indicates a suspicious sample, and represents light tar oils. Water is estimated by agitating the sample with half its volume of a saturated solution of salt, the loss of volume indicates the amount of water originally present. To ascertain the quality of crude carbolic acid and probable yield of crystallized phenol, the following method of Lowe (Allen, Com. Org. Anal., 3d ed., vol. ii., Part ii. p. 252) is used. One hundred cubic centimetres are distilled, and the distillate collected in graduated tubes. Water first distils, and is followed by an oily fluid; this is allowed to stand, when the volume of water is read off. If the oily liquid floats on the water, it contains light oil of tar. It should be heavier than water, in which case it may be regarded as hydrated acid containing about fifty per cent. of real carbolic acid. The next portion of the distillate consists of anhydrous acid, and when it measures 62.5 per cent. the receiver is again changed. The residue in the retort consists wholly of cresylic acid and still higher homologues of carbolic acid. The 62.5 per cent. of anhydrous acid contains variable proportions of carbolic and cresylic acid. These may be approximately determined by ascertaining the solidifying point, which should be between 15.5° and 24° C., and by making, with known proportions of carbolic and cresylic acids, a standard sample that will have the same solidifying point.

(c) *Naphthalene.*—The assay of this substance generally consists in submitting about twenty-five grammes, wrapped in several folds of filter or bibulous paper, to pressure in a copying-press until the exudation of any oil ceases, when the cake is again weighed, and if desirable, distilled from a small retort. Good samples should not distil below 210°, and should yield ninety per cent. of distillate before the temperature exceeds 225° C. Upon warming sublimed naphthalene with pure sulphuric acid in a test-tube, the solution should remain colorless. If one per cent. of impurity is present, a decided pinkish tint is observed, which is darker the greater the amount. The determination of the specific gravity, the melting point (79° C.), and the boiling point (216° to 218° C.) are made by the usual methods.

(d) *Creosote Oils.*—The characteristics of this fraction were previously indicated. The specific gravity is determined either by the bottle or hydrometer; in cases where the sample contains much naphthalene, the specific gravity bottle is filled and the contents allowed to become solid, when the stopper is worked in. A sample should become quite clear upon warming to about 38° C., and ought not become turbid till cooled to 32° C. The liquefying point is determined by transferring a sample of the oil to a test-tube immersing a thermometer, and warming gently till it becomes liquid. The point of turbidity is similarly observed, by allowing the tube to cool spontaneously. For the determination of the naphthalene, one hundred grammes are chilled to 45° C. in a small beaker, when it is transferred to a cloth filter, placed in a funnel provided with means for cooling to 4.5° dur-

ing filtration. The filter and contents are removed and quickly pressed between bibulous paper in a copying-press, when the cake is pressed and weighed.

(e) *Anthracene.*—Commercial anthracene contains a very variable percentage of real anthracene, the usual proportions being from thirty to forty per cent., though formerly fifteen per cent. was common, and special lots now assay over eighty per cent. The value of anthracene does not entirely depend upon the amount of real anthracene alone, but also upon the freedom from objectionable impurities. In testing for *paraffine*, ten grammes of the sample are taken and treated with two hundred grammes of concentrated sulphuric acid, heated on a water-bath for about ten minutes, or until the anthracene is dissolved, when any *paraffine* will rise to the surface in oily globules. The solution is now poured cautiously into a tall beaker containing five hundred cubic centimetres of water, stirred, and cooled, when the paraffine rises and solidifies on the surface; it is washed with water, dried between filter-paper, and weighed.

By the conversion of anthracene into *anthraquinone* the most satisfactory method of assaying is obtained. (See Allen, Com. Org. Anal., 3d ed., vol. ii., Part ii. p. 230.) One gramme of the carefully sampled specimen is placed in a flask holding five hundred cubic centimetres, forty-five cubic centimetres of the very strongest glacial acetic acid is added, and an inverted condenser, or long glass tube adapted to the flask. The liquid is then brought to the boiling point, and, while boiling, the chromic acid solution is added to it gradually, drop by drop, by means of a tapped funnel passing through the india-rubber stopper in the flask, or inserted in the top of the vertical condenser. The chromic acid solution is prepared by dissolving fifteen grammes of crystallized chromic anhydride in ten cubic centimetres of water and ten of glacial acetic acid. The addition of the oxidizing agent should occupy two hours, and the contents of the flask should be kept in constant ebullition for two hours longer. The flask is then left for twelve hours, when the contents should be diluted with four hundred cubic centimetres of cold water, and allowed to rest for three hours longer. The precipitated anthraquinone is filtered off, and well washed on the filter with cold water, and with a boiling one per cent. solution of caustic soda and again with water. The anthraquinone is rinsed from the filter into a small dish, the water evaporated off, the residue dried at 100° C., and weighed. The following after-treatment is now universally employed: to the weighed residue ten times its weight of fuming sulphuric acid is added, and the whole heated to 100° C. on a water-bath for ten minutes, after which it is left in a damp place for twelve hours to absorb water, when two hundred cubic centimetres of water are added; the precipitat[illegible] anthraquinone filtered off, washed with water, and then with one hu[illegible] cubic centimetres of a one per cent. boiling solution of caustic soda, [illegible]ly with boiling water, transferred to a dish, any water being eva[illegible] off, and the whole dried at 100° C. and weighed. The weight [illegible] one multiplied by the factor, .856, gives the real anthra[illegible]t of the sample.

[illegible] *Tar and Pitch.*—Nicol (Z. a. Chemie, xiv. p. 318) treats [illegible] in a small retort, receiving the vapors in a U tube kept at [illegible] more volatile products do not condense, but the anthracene [illegible]ocarbons do. When coking has taken place, the process is [illegible]he neck cut off, pounded, and the powder added to the dis[illegible] whole is then dissolved in glacial acetic acid and subjected to

25

oxidation with chromic acid as above described. Watson Smith does not recommend the use of such a small quantity (twenty grammes); he employs a similar method, but operates upon, at least, a litre, rejecting the portion distilling just before the coking. The anthracene oil is well mixed and an aliquot part employed.

(*f*) *Pitch.*—The uses to which this residue is put are such that an elaborate method of valuation is unnecessary, although the method for asphalt is applicable. To distinguish between the two, one gramme of the sample is treated with five cubic centimetres of petroleum-spirit, and rapidly shaken. The mixture is filtered, and five to six drops of the filtrate diluted to five cubic centimetres with petroleum-spirit, when a greenish fluorescence will be noticed in the case of tar. Five cubic centimetres of rectified spirit should then be added, the mixture shaken and allowed to stand. The upper layer will consist of strongly-colored petroleum-spirit, while the lower layer of alcohol will have a golden-yellow color if coal-tar is present. In the case of mineral asphalt, the alcohol is faintly straw-yellow and often colorless.

3. VALUATION OF AMMONIA-LIQUOR.—Ordinarily, the Twaddle hydrometer is employed to determine the strength of ammonia-liquor; every degree of the instrument is taken to represent such an amount of ammonia in the liquor so tested that one gallon will require two ounces of concentrated oil of vitriol to saturate it; by this means a liquor of 5° Tw. would be known as "Ten-ounce," 4° Tw. would be "Eight-ounce," etc. These results are fallacious, owing to the presence of substances which cause a false strength to be indicated.

The most accurate and practical method consists in decomposing ten cubic centimetres of the gas-liquor to be assayed in a flask by means of a solution of caustic soda, applying heat, and collecting the vapors of ammonia evolved in a known quantity of normal sulphuric acid contained in another flask suitably connected; the ammonia vapors neutralize part of this acid, and that which remains uncombined is exactly neutralized in the presence of litmus solution with normal ammonia, when the percentage of ammonia is at once determined.

4. ANALYSIS OF ILLUMINATING GAS.—The analysis of illuminating gas can be most conveniently carried out for technical purposes with the absorption apparatus devised by Hempel, although there are several other forms in use which give results equally, and in some cases more, accurate. Hempel employs, for measuring the gas under examination, a cylindrical tube, similar to an ordinary burette, graduated to one hundred cubic centimetres in one-fifths, and mounted in an iron base. This burette is open at the top, and at the bottom by means of a side-tube. Another tube similar to the first, but without graduations, is used as a "level-tube," and is connected to the burette by a caoutchouc tube of sufficient length that the level-tube can be raised to the height of the former without inconvenience. There are also used pipettes, the ordinary form of which consists of two glass bulbs, connected by means of capillary tubes, and fastened to a board provided with openings to accommodate the bulbs, and mounted upon a foot. From one of the bulbs a siphon-shaped tube extends, which projects a short distance beyond the stand, and to which is attached a caoutchouc tube connecting it with the top of the burette. The pipettes contain the several liquids and solid reagents necessary to absorb the constituents of the gas. Besides the simple form above mentioned, there is a "tubulated

absorption pipette," so made as to allow the introduction of solids, and which can be readily altered to a pipette for the generation and retention of gases, as hydrogen and carbon dioxide, by the means of zinc or calcite respectively, the acid required for the liberation of the gas being contained in the second bulb.

Another form is the "compound absorption pipette," which is employed for containing the reagents readily decomposed upon exposure to the atmosphere, or which give off noxious vapors.

The method of operating is as follows: The level-tube, previously filled with water, is raised until the gas-burette is completely filled, when it is connected by means of a caoutchouc tube to the "aspirating-tube," or source of the gas, when the level-tube is lowered, and the water flows out, causing the gas to take its place in the burette; one hundred cubic centimetres are obtained, which is noticed by causing the water-level in each tube to coincide with the 100-cubic-centimetre mark on the lower end of the burette. The absorption of the several constituents takes place by connecting the top of the burette to the end of the siphon-shaped tube before mentioned, when the level-tube is raised, and the gas is forced from the burette into the bulb of the pipette, the absorbent in which has been forced into the second bulb. When all the gas has passed over, compressors are applied and the pipette detached, and very gently agitated from two to five minutes, in which time the absorption will be complete; the pipette is again attached, the level-tube lowered, when the remainder of the gas is drawn back to the burette, which is closed, the water-level in each brought to coincide, and the reading taken. The difference between this reading and the original volume of gas taken is the volume absorbed. One constituent after another is in this way withdrawn by using pipettes containing solutions having affinity for the several gas components, as indicated below:

| | |
|---|---|
| Carbon dioxide ($CO_2$). | Solution of potassic hydrate. |
| Ethylene ($C_2H_4$).<br>Propylene ($C_3H_6$).<br>Butylene ($C_4H_8$). | Fuming sulphuric acid or bromine-water. After agitation, the vapors remaining in the gas are removed by contact with potassic hydrate solution. |
| Benzene vapor ($C_6H_6$). | Fuming nitric acid may be employed, and the nitrous vapor remaining removed by agitation in the potassic hydrate pipette, or absolute alcohol is used. |
| Oxygen (O). | An alkaline solution of pyrogallol, or phosphorus chips in the presence of water, can be used. |
| Carbon monoxide (CO). | A solution of cuprous chloride in hydrochloric acid or ammonia. |
| Hydrogen (H).<br>Methane ($CH_4$).<br>Nitrogen (N). | Residue, unabsorbed. Constituents determined by combustion, mixing the residual gas with air, and passing the mixture over palladium sponge. |

## V. Bibliography and Statistics.

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## STATISTICS.

1. OF COAL CARBONIZED IN GAS-MAKING.—Lunge (Coal-Tar and Ammonia, 2d ed., pp. 12 and 13) gives several estimates of the amount of coal distilled for gas-making in Great Britain and Ireland, varying from nine million to twelve million tons per annum. The annual distillation for the same purpose in Germany is given at two million tons. For the United States, no estimates of the coal used in gas-making can be found.

2. OF COAL CARBONIZED IN COKE-OVENS.—According to "Mineral Resources of the United States for 1898," the statistics of coke-production in recent years were as follows:

| | 1896. | 1897. | 1898. |
|---|---|---|---|
| Coal used, short tons | 18,694,422 | 20,907,319 | 25,249,570 |
| Coke produced, short tons | 11,788,773 | 13,288,984 | 16,047,209 |
| Average percentage yield | 63 | 63.5 | 63.6 |
| Value of coke produced | $21,660,729 | $22,102,514 | $25,586,699 |

Of this amount, two-thirds is produced in the State of Pennsylvania, while West Virginia, Alabama, Virginia, and Colorado follow in the order named. The total number of coke-ovens in the United States at the end of 1898 was 48,447.

The present annual production of coke in Great Britain is said to be 21,000,000 tons, requiring the carbonization of 35,000,000 tons of coal.

3. BY-PRODUCT COKE-OVENS IN THE UNITED STATES.—According to "Mineral Resources of the United States for 1898," there were at the end of that year the following number of by-product ovens completed and building:

| | |
|---|---|
| Completed | 280 Semet-Solvay ovens. |
| " | 180 Otto-Hoffmann ovens. |
| " | 90 Newton-Chambers ovens. |
| " | 3 Slocum ovens. |
| Building | 500 Otto-Hoffmann ovens. |

4. OF COAL-TAR PRODUCTION.—Gallois * gives the following as the production of gas-tar in some of the principal European countries for the year 1883 :

| | Number of gas-works. | Coal-tar produced. |
|---|---|---|
| Great Britain | 452 | 450,000 tons. |
| Germany | 481 | 85,000 " |
| France | 601 | 75,000 " |
| Belgium | | 50,000 " |
| Holland | | 15,000 " |
| Total | | 675,000 " |

Other estimates of the production of coal-tar in Great Britain and Ireland as quoted by Lunge vary from 450,000 tons to 750,000 tons. That of Mr. Wilton, of the Beckton Tar-works, putting the quantity of tar distilled in 1885 at 120,000,000 gallons, averaging twelve pounds, or about 643,000 tons, would seem to be near the mean of these estimates.

The same author,† from information gathered by himself, puts the production of coal-tar for 1886 in Holland at 20,000 to 22,000 tons, in Belgium at about 30,000 tons, and in the United States at 120,000 tons, of which some 60,000 tons are distilled, 37,000 tons are employed for manufacturing roofing-paper, roof-coating, etc., and some 23,000 tons are used up in the raw state.

4. OF COAL-TAR DISTILLATION PRODUCTS.—The estimate of Mr. Wilton of the coal-tar production of the United Kingdom for 1885 above quoted includes the following additional details :

| | | |
|---|---|---|
| Ammoniacal liquor from tar alone | 3,600,000 gallons | = 1200 tons of sulphate. |
| Carbolic acid (crude) | 600,000 " | |
| Creosote oil | 21,600,000 " | |
| Of this, there was liquid creosote | 10,800,000 " | |
| Of this, there were creosote salts (crude naphthalene, etc.) | 56,620 tons. | |
| Corresponding to pure naphthalene | 25,310 " | |
| Green oil | 20,400,000 gallons. | |
| Benzol and toluol | 1,500,000 " | |
| Solvent naphtha | 620,000 " | |
| Anthracene (pure) | 3,420 tons. | |
| Pitch | 396,000 " | |

The German importations of the crude coal-tar and coal-tar products during the years 1892 and 1893 were:

| | 1892. | 1893. |
|---|---|---|
| Coal-tar, metric centners | 368,904 | 397,217 |
| Value in marks | 2,029,000 | 1,787,000 |
| Coal-tar pitch, metric centners | 113,078 | 877,689 |
| Value in marks | 1,583,000 | 3,888,000 |
| Light tar oils, metric centners | 56,833 | 74,726 |
| Value in marks | 4,831,000 | 4,110,000 |
| Heavy tar oils, metric centners | 29,552 | 14,819 |
| Value in marks | 443,000 | 296,000 |

5. PRODUCTION OF SULPHATE OF AMMONIA.—The production for Great Britain and Ireland much exceeds that of all other countries com-

* Lunge, Coal-Tar and Ammonia, 2d ed., p. 13.
† Ibid., p. 15.

bined. The following table shows the amount produced in recent years and the sources from which it is obtained:

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| From gas-works, tons | 127,500 | 133,000 | 130,000 | 133,000 |
| From iron-works, tons | 16,500 | 18,000 | 17,700 | 18,700 |
| From shale-works, tons | 38,000 | 37,000 | 37,300 | 37,300 |
| From coke- and carbonizing-works, tons | 9,000 | 10,000 | 11,500 | 13,000 |
| Total | 191,000 | 198,000 | 196,500 | 202,000 |

(Soc. Chem. Ind. Journ., 1900, p. 87.)

Lunge states (Coal-Tar and Ammonia, 2d ed., p. 667) that Germany produces about 10,000 tons of sulphate of ammonia per annum, France produces about 12,500 tons, Holland and Belgium about 3,000 tons, and the United States about 11,000 tons per annum.

# CHAPTER XII.

## THE ARTIFICIAL COLORING MATTERS.

### I. Raw Materials.

1. HYDROCARBONS.—*Benzene Series.*—In the manufacture of the artificial coloring matters, the hydrocarbons which find application as raw materials are limited mainly to benzene, naphthalene, and anthracene, their homologues and derivatives; of which, probably, benzene is the most important.

The benzene series is as follows:

| | Boiling-point. | Specific gravity. |
|---|---|---|
| Benzene, $C_6H_6$ | 80.4° C. | .884 at 15° C. |
| Toluene, $C_6H_5.CH_3$ | 110° C. | .869 at 15° C. |
| Xylene, $C_6H_4.(CH_3)_2$ { *o*-Xylene | 142° C. | .893 at 0° C. |
| Xylene, $C_6H_4.(CH_3)_2$ { *m*-Xylene | 139° C. | .881 at 0° C. |
| Xylene, $C_6H_4.(CH_3)_2$ { *p*-Xylene | 138° C. | .880 at 0° C. |
| Pseudocumene, $C_6H_3.(CH_3)_3$ | 169.5° C. | .895 at 0° C. |
| Mesitylene, $C_6H_3.(CH_3)_3$ | 165° C. | .865 at 14° C. |
| Durene, $C_6H_2.(CH_3)_4$. (Fuses at 79°–80° C.) | 192° C. | . . . . . |
| Pentamethylbenzene, $C_6H.(CH_3)_5$. (Fuses at 51.5° C.) | 231° C. | . . . . . |
| Hexamethylbenzene, $C_6(CH_3)_6$. (Fuses at 166° C.) | 265° C. | . . . . . |

Of which only the first three are employed to any extent.

Benzene has been described in a previous chapter (see Tar Distillation), but for the manufacture of colors an explanation is necessary; the name *benzene*, chemically speaking, does not refer to the light fractions obtained from petroleum, but applies solely to the substance distilled from coal-tar; boiling at 80.4° to 81° C., having a specific gravity of .899° at 0°, with the definite composition $C_6H_6$. The term *benzol*, on the other hand, is not given to a definite compound, but to a mixture of *benzene* with variable quantities of *toluene* and *xylene*, with other homologues of the same series. The quantity of these homologous bodies contained have an influence upon the use to which the aniline oil obtained (by subsequent treatment of the benzol) can be put.

The pure benzene, free from the high boiling homologues, is successively converted through several processes to dimethylaniline, which is the base of the valuable methyl-violets. For the fuchsine process, benzol, seventy-five per cent. of which distils between 80° and 100° C. (containing toluene), is employed, producing aniline, seventy-five per cent. of which distils between 180° and 190° C. High-boiling benzol, 115° to 120° C., yields aniline, which is the starting-point for the production of the beautiful series of xylidine scarlets; the introduction, however, of pure xylene has served to displace the above. Allen states (Commercial Organic Analysis, 2d ed., vol. ii. p. 489), "*Ninety per cent. benzol* is a product of which ninety per cent. by volume distils before the thermometer rises above 100° C. A good sample should not begin to distil under 80° C., and should not yield more than twenty to thirty per cent. at 85°, or much more than ninety per cent. at

100° C. It should wholly distil below 120° C. An excessive distillate—*e.g.*, thirty-five to forty per cent. at 85° C.—indicates a larger proportion of carbon bisulphide or light hydrocarbons than is desirable.

"The actual percentage composition of a ninety per cent. benzol of good quality is about seventy of benzene, twenty-four of toluene, including a little xylene, and four to six of carbon bisulphide and light hydrocarbons. The proportion of real benzene may fall as low as sixty or rise as high as seventy-five per cent. Ninety per cent. benzol should be colorless and free from opalescence."

"*Fifty per cent. benzol*, often called 50/90 benzol, is a product of which fifty per cent. by volume distils over at a temperature not exceeding 100° C., and forty per cent. more below 120°. It should wholly distil below 130°."

"*Thirty per cent. benzol* is a product of which thirty per cent. distils below 100°, about sixty per cent. more passing over between 100° and 120°. It consists chiefly of toluene and xylene, with small proportions of benzene, cumene, etc."

The following table from Schultz (Steinkohlentheers) indicates the general properties of the three commercial benzols above described when subjected to distillation:

| | Thirty per cent. | Fifty per cent. | Ninety per cent. |
|---|---|---|---|
| To 85° | 0 | 0 | 25 |
| " 90° | 2 | 4 | 70 |
| " 95° | 12 | 26 | 83 |
| " 100° | 30 | 50 | 90 |
| " 105° | 42 | 62 | 94 |
| " 110° | 70 | 71 | 97 |
| " 115° | 82 | 82 | 98 |
| " 120° | 90 | 90 | 99 |

The theoretical quantities of commercially applicable products from benzol are:

For 100 parts, 157.6 parts nitrobenzol.
" " " 119.2 " aniline.
" " " 215.3 " dinitrobenzol.
" " " 155.1 " dimethylaniline.
" " " 191.0 " diethylaniline.

*Toluene*, or *Methylbenzene*, $C_6H_5.CH_3$, is obtained by careful distillation of coal-tar benzols, and can be obtained from the balsam of tolu and other sources. It is quite similar in its properties to benzene; fluid at ordinary temperatures, and when pure boils between 110° and 111° C. Specific gravity .869. It is employed for the production of nitrotoluene, toluidine, benzylchloride, benzalchloride, and benzaldehyde,—the base of a valuable series of green colors. The theoretical yield of commercial products from toluene are as follows:

For 100 parts, 148.9 parts nitrotoluene.
" " " 116.3 " toluidine.
" " " 115.3 " benzaldehyde.

*Xylene*, or *Dimethylbenzene*, $C_6H_4.(CH_3)_2$, exists under similar conditions

to toluene, and is found in coal-tar. There are three xylenes, the ortho-, meta-, and para-, the second being most abundantly obtained. Owing to the slight difference between their respective boiling-points, a commercial separation by distillation is practically impossible.

The annexed table gives the nature and behavior of the three isomeric hydrocarbons mentioned.

| | | Ortho-xylene. | Meta-xylene. | Para-xylene. |
|---|---|---|---|---|
| Melting point | | Fluid. | Fluid. | 15° C. |
| Boiling-point | | 141° to 142° C. | 139° C. | 137.5° to 138° C. |
| Specific gravity | | . . . . . . . | .8668 at 19° C. | .8621 at 19.5° C. |
| Oxidized with | Dilute nitric acid | o-Toluic acid, melting point 102° C. | m-Toluic acid, melting point 160° C. | p-Toluic acid, melting point 178° C. |
| | Permanganate | Phthalic acid. | Isophthalic acid. | Terephthalic acid |
| | Chromic acid | Decomposed. | Isophthalic acid. | |
| Sulphuric acid (66° Bé.) | | Sulphonic acid. | Two sulphonic acids. | No change. |
| Sulphuric acid (fuming) | | Sulphonic acid. | Two sulphonic acids. | Sulphonic acid. |
| Melting point of the sulphochloride | | 52° C. | (a) 34° C., (b) liquid. | 26° C. |
| Melting point of the sulphamide | | 144° C. | (a) 137° C., (b) 96° C. | 148° C. |

From Schultz, "Steinkohlentheers."

*Naphthalene Series.*—*Naphthalene*, $C_{10}H_8$, as a raw material, enters largely into the production of the extensive series of azo-coloring matters, and for such use it is converted into intermediary products, of which the alpha- and beta-naphthols are the most familiar. The occurrence, properties, and production of naphthalene are referred to on page 378.

*Methyl-naphthalene*, $C_{10}H_7CH_3$.—Two isomers exist in coal-tar, and can be separated from that fraction of the distillate, boiling at from 220° to 270° C. The first of these is a liquid boiling at 243° C.; specific gravity 1.0287 at 11.5°. The second is a solid, looking like naphthalene, melting at 32.5° C. and boiling at 242° C.

*Ethyl-naphthalene*, $C_{12}H_{12}$. — Two isomers, α- and β-, are known. α-Ethyl-naphthalene, produced from α-brom-naphthalene and ethyl-bromide, and distilled in vacuum, boils at from 257° to 259.5° C. β-Ethyl-naphthalene, from β-brom-naphthalene, ethyl bromide, and sodium. Boils at from 250° to 251° C.

*Diphenyl*, $C_{12}H_{10}$, has been found in coal-tar, and is readily obtained when benzene vapors are passed through a red-hot tube. It is insoluble in water, soluble in hot alcohol and in ether. It forms large colorless scales, melting at 71° C. and boiling at 254° C. Oxidized by chromic acid, it yields benzoic acid.

*Stilbene*, $C_{14}H_{12}$.—This compound, which is diphenylethylene ($C_6H_5$.-$CH = CH.C_6H_5$), is formed when toluene or dibenzyl is led over heated lead oxide. It crystallizes in colorless scales, melting at 125° C. Forms the basis of numerous important dyes.

*Anthracene Series.*—*Anthracene*, $C_{14}H_{10}$, reference to which has been made in the previous chapter, is employed for the production of alizarine and allied bodies, the successful introduction of which caused a revolution in the processes of dyeing, and made useless for the time great areas of land

which were devoted to the culture of madder. Anthracene, as it occurs in commerce, is rarely pure, being made up of a very large number of hydrocarbons, several of which have not been investigated. The following may be mentioned:

*Methyl-anthracene*, $C_{15}H_{12}$, closely resembles anthracene. It differs from that body in having a methyl group substituted for an H atom of one of the benzene rings. It occurs in coal-tar in small quantity, and owing to the high boiling-point, over 360° C., it is found in the anthracene. Crystallizes in pale-yellow leaflets, melting at 199° to 200°.

*Phenyl-anthracene*, $C_{20}H_{14}$, is formed when phenyl-anthranol or cœruleïn is heated with zinc-dust. Slightly soluble in hot alcohol, ether, benzene, carbon bisulphide, and chloroform, and upon cooling, crystallizes from the above solvents in yellow plates, melting at 152° to 153° C. The solutions have a blue fluorescence.

*Fluorene*, or *Diphenylen-methane*, $C_{13}H_{10}$, is found in coal-tar, and can be obtained by passing diphenylmethane through a combustion-tube heated to redness; it can also be obtained by distilling diphenyleneketone over heated zinc-dust, or by heating the same substance with hydriodic acid and phosphorus from 150° to 160°. Very soluble in hot alcohol, less in the cold; crystallizes in colorless plates having a violet fluorescence. Melts at 113° C., boils at 295° C.

*Phenanthrene*, $C_{14}H_{10}$.—This hydrocarbon is isomeric with anthracene, is found with it, and forms a large part of, the last fraction of coal-tar. Compared with anthracene, the melting point is considerably lower, while the boiling-points are somewhat closer. It is much more soluble in alcohol, by which means a separation is effected; the low melting point materially assisting. Crystallizes in colorless, shining plates, melting at 100° and boiling at 340°, insoluble in water, but soluble in fifty parts of alcohol in the cold, and in ten parts on boiling; easily soluble in ether and benzene. It imparts a blue fluorescence when dissolved. When oxidized, phenanthrenquinone is formed. Technically, but little use is made of it, being chiefly employed in the oil-baths for alkali melts, heating autoclaves, subliming phthalic anhydride, etc.

*Fluoranthene*, $C_{15}H_{10}$, occurs in the highest boiling tar fractions; crystallizes in needles; melts at 109°.

*Pseudophenanthrene*, $C_{16}H_{12}$, is found in crude anthracene, and crystallizes in large glistening plates, which melt at 115°. *Pyrene*, $C_{16}H_{10}$, *Retene*, $C_{18}H_{18}$, *Chrysene*, $C_{18}H_{12}$, and *Picene*, $C_{22}H_{14}$, are bodies which occur in the highest fractions with fluoranthene, and cannot be classed as raw materials, —no technical importance being attached to them.

2. HALOGEN DERIVATIVES.—*From Benzene.*—The following table of the halogen derivatives of benzene indicates those whose constitution is known. They are produced by the action of the halogens upon the hydrocarbons directly, or through the action of the halogen compounds of phosphorus upon phenols and aromatic alcohols. Two classes are produced, substitution and addition compounds. The former occur under ordinary conditions, while the latter are formed when the reaction takes place in direct sunlight. Of the two, the substitution products are the more stable, the addition products being easily decomposed.

The following table gives the formulas of the several halogen derivatives of benzene and the boiling-points of the more important of the several isomeric compounds:

| Halogen substitution products of benzene. | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_6$ | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $C_6H_5$ | Cl | 183° | ... | ... | Br | 154° | ... | ... | I | 185° | ... |
| $C_6H_4$ | $Cl_2$ | 179° | 172° | 173° | $Br_2$ | 224° | 219° | 219° | $I_2$ | 277° | 285° |
| $C_6H_3$ | $Cl_3$ | 213° | 208° | 218° | $Br_3$ | 276° | 278° | ... | $I_3$ | ... | ... |
| $C_6H_2$ | $Cl_4$ | 246° | 246° | 254° | $Br_4$ | 329° | ... | ... | $I_4$ | ... | ... |
| $C_6H$ | $Cl_5$ | 276° | ... | ... | $Br_5$ | ... | ... | ... | $I_5$ | ... | ... |
| $C_6$ | $Cl_6$ | 332° | ... | ... | $Br_6$ | ... | ... | ... | $I_6$ | ... | ... |

*From Toluene.*—(1) *Benzyl-chloride* (*Chlorbenzyl*), $C_6H_5.CH_2.Cl$, results from the action of hydrochloric acid upon benzyl alcohol ($C_6H_5.CH_2.OH$), or by acting on boiling toluene with chlorine, this method being the one most generally used; the product is washed with water containing a little alkali, when it is freed from impurities by distillation. It is a colorless fluid, specific gravity 1.113, boils at 179°, insoluble in water, but soluble in alcohol and ether, and possesses an exceedingly penetrating odor, acting upon the eyes and mucous membrane of the nose. Technically, it finds considerable application in the color industry.

(2) *Benzal-chloride* (*Benzidene Dichloride*), $C_6H_5.CH.Cl_2$.—Formed when chlorine acts upon boiling benzyl-chloride, or when phosphorus penta-chloride acts upon benzaldehyde. It is a colorless liquid, having ordinarily but little odor, but upon the application of heat gives off a vapor producing effects similar to the preceding. Boils at 206° to 207°; specific gravity at 16° 1.295.

(3) *Benzo-trichloride*, $C_6H_5.C.Cl_3$, is obtained by acting with chlorine upon boiling toluene until no further increase in weight takes place, when it is washed in water containing alkali, dried, and distilled in a vacuum. Boils at 213° to 214°; specific gravity 1.38 at 14°. It has a penetrating odor, and is highly refractive.

*Bromine Derivatives of Xylene.*—These are obtained when bromine is allowed to act upon the hydrocarbon or its isomers, or upon brominated compounds of the same, with or without the presence of iodine. They find no application industrially.

*Halogen Derivatives of Naphthalene.*—(1) *Naphthalene Dichloride*, $C_{10}H_8Cl_2$, is a liquid, easily decomposed; produced as an addition compound by the action of chlorine gas upon naphthalene.

(2) *Naphthalene Tetrachloride*, $C_{10}H_8.Cl_4$.—This substance is manufactured in large quantities by passing chlorine gas through the melted hydrocarbon in a suitable apparatus, or by grinding the naphthalene to a paste with water and intimately kneading therein sodium or potassium chlorate, moulding into balls, and drying, after which they are immersed in concentrated hydrochloric acid. It crystallizes from chloroform in large rhombohedra, melting at 182°, and when boiled with nitric acid is converted into phthalic acid, which is the chief product obtained from it.

(3) *α-Brom-naphthalene*, $C_{10}H_7.Br$.—Formed by the direct bromination of the hydrocarbon, or by the substitution of bromine for the amido group in brom-α-naphthylamine. It is a liquid, boiling at 277°; specific gravity 1.503 at 12°. Insoluble in water, soluble in alcohol and ether.

(4) *β-Naphthyl-chloride*, $C_{10}H_7.CH_2Cl$, is formed when chlorine acts upon β-methyl-naphthalene at a temperature of 240° to 250°. Melts at 47°, boils at 168°.

(5) *β-Naphthyl-bromide*, $C_{10}H_7.CH_2Br$.—Formed when the vapor of bromine with $CO_2$ gas is brought in contact with β-methyl-naphthalene, heated to 240°. Crystallizes from alcohol in white plates, which melt at 56°.

*Anthracene Derivatives.*—(1) *Monochlor-anthracene*, $C_{14}H_9.Cl$.—When dichlor-anthracene is heated hydrochloric acid is evolved, having the monochlor derivative. Soluble in alcohol, ether, carbon bisulphide, and benzene. Crystallizes in yellow needles, melting at 103°.

(2) *Dichlor-anthracene*, $C_{14}H_8.Cl_2$, is produced when anthracene is allowed to remain in contact with chlorine, or when the monochlor derivative is similarly treated, being maintained at a temperature of 100°. Freely soluble in benzene, but not readily in alcohol or ether. Forms beautiful yellow lustrous needles, which melt at 209°. Treated with sulphuric acid at a low temperature, dichlor-anthracene-sulphonic acid occurs in solution; this, when heated, yields sulphurous acid, hydrochloric acid, and the anthraquinone-disulphonic acid, which is the immediate base of the artificial alizarine.

(3) *Dibrom-anthracene*, $C_{14}H_8Br_2$.—Upon agitating bromine with a solution of anthracene in carbon bisulphide this derivative is formed. Difficultly soluble in alcohol, ether, and benzene; hot toluene or xylene answer best. Crystallizes in gold-yellow needles, melting at 221°, and subliming without decomposition.

3. NITRO- DERIVATIVES.—By the action of nitric acid upon the hydrocarbons nitro- derivatives are obtained, and one of the most important of these—nitrobenzene—is manufactured in very large quantities for use in the color industry.

(1) *Nitrobenzene*, $C_6H_5.NO_2$, was discovered by Mitscherlich, who obtained it by heating benzene or benzoic acid with fuming nitric acid. It was first brought into trade, bearing the name "oil of mirbane" (artificial oil of bitter almonds), by Collas, and in 1847 a patent for its manufacture from coal-tar was granted to Mansfield. It is obtained by adding a cooled mixture of concentrated sulphuric and nitric acid (150 : 100) to the hydrocarbon and agitating, taking care that the temperature does not go above 50° C. After the addition of the acid is complete, heat is applied, and it is again agitated. The oily layer is removed, washed with dilute alkali, dried, and distilled. Nitrobenzene, when pure, is a pale-yellow fluid, strongly refractive, having the odor of bitter almonds, and a sweet, though burning, taste. Specific gravity 1.208 at 15°; boils at 206° to 207°, and when the temperature is reduced it crystallizes in large needles, which melt at +3°. Nearly insoluble in water, though with alcohol, ether, and benzene it is readily soluble. It is exceedingly stable, and even at a boiling temperature it is not acted upon by either bromine or chlorine. It is poisonous, and, according to Roscoe and Schorlemmer (vol. iii. pt. iii.), "especially when the vapor is inhaled; it produces a burning sensation in the mouth, nausea and giddiness, also cyanosis of the lips and face, and in serious cases, which [fre]quently end fatally, symptoms of a general depression."

(2) *Dinitrobenzene*, $C_6H_4(NO_2)_2$.—Three isomers of this derivative exist, [bei]ng obtained when benzene is nitrated with the concentrated acids, as in [th]e preceding case, but instead of being cooled is boiled for a short time, [t]hen the product is washed with water, pressed, dissolved in alcohol, from [w]hich the meta-nitro body crystallizes, followed upon standing by the paranitro compound. Upon distilling the alcohol remaining in the mother-

liquors from the *para-* compound a further yield of the *meta-* body is obtained, finally the *ortho-dinitrobenzene,* which occurs in small quantity, crystallizes, and is purified by treatment with acetic acid, from which it is deposited in needles, having a melting point of 117.9°. The *para-* compound occurs in monoclinic needles, melting at 172°, and subliming. The *meta-* compound finds technical application in the production of chrysoidine and Bismark brown, and is manufactured on a large scale by adding a mixture of one hundred kilos. nitric acid (specific gravity 1.38) and one hundred and fifty-six kilos. sulphuric acid (specific gravity 1.84) to one hundred kilos. of benzene. When the reaction is over, a separation of the acids (which can be used again) from the product occurs; commercially, the product is washed with warm and cold water, further purification being unnecessary. It crystallizes in needles or rhombic tables, which melt at 89.8°, boiling at 297°. Difficultly soluble in warm water, easily in ether and alcohol.

*Nitrotoluene.*—(1) *Nitrotoluene,* $C_6H_4(NO_2)CH_3$, occurs in three isomers. The *ortho-* derivative is a liquid boiling at 223°, and at 23.5° has a specific gravity of 1.162. Does not become solid at 20°. The *meta-* derivative melts at 16°, boils at 230° to 231°. Specific gravity at 22° 1.168. *Para-*nitrotoluene, melting point 54°, distilling unchanged at 236°, occurs in colorless prisms. Nitrotoluene, consisting more or less of a mixture of the above, is manufactured in large quantities and in the same manner as for nitrobenzene. Ten parts of toluene are mixed, and continually agitated with eleven parts of nitric acid (specific gravity 1.22) and one part sulphuric acid (specific gravity 1.33). The product is treated with water, and afterwards with caustic alkali; distilled to remove uncombined toluene, and finally distilled with superheated steam. When fractionated, that part passing over at 230° yields, when purified, para-nitrotoluene, and is employed in the production of toluidine, tolidine, and fuchsine. The fraction between 222° and 223° is nearly all ortho-nitrotoluene.

(2) *Dinitrotoluenes,* $C_6H_3(NO_2)_2.CH_3$.—α- or ordinary dinitrotoluene is produced when toluene is added to a mixture of fuming nitric and sulphuric acids and boiled; ortho-nitrotoluene is employed for the manufacture also. Crystallizes in needles, which melt at 70.5°; insoluble in water, little soluble in alcohol, ether, or carbon bisulphide. β-dinitrotoluene, isomeric with the above, is produced under similar conditions; or it can be made by replacing the amido group of dinitroparatoluidine with hydrogen. Crystallizes in golden-yellow needles; melting point 61.5°.

*Trinitrotoluene,* $C_6H_2.(NO_2)_3CH_3$.—Produced by the action of nitric and sulphuric acids upon toluene, or dinotrotoluene, and heating for several days. α-Trinitrotoluene is soluble in alcohol, crystallizing from it in beautiful needles, which melt at 82°. β-Trinitrotoluene crystallizes from acetone in transparent prisms, which melt at 112°, while from alcohol it forms plates or flat white needles. γ-Trinitrotoluene is deposited from acetone in small hexagonal crystals, melting at 104°.

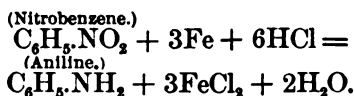
*Mononitronaphthalene,* $C_{10}H_7.NO_2$.—Two isomers exist; the α- compound is produced when ten parts naphthalene, eight parts nitric acid (specific gravity 1.4), and ten parts sulphuric acid (specific gravity 1.84) are combined in a nitrobenzene apparatus. The naphthalene is added in small portions and continually stirred. The product is washed with water, and freed from acid by treatment with alkali. Insoluble in water, easily in benzene, carbon bisulphide, ether, and alcohol. Crystallizing in yellow needles, melting at

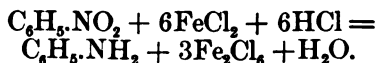
61°, boiling at 304°. The β- compound is produced when γ-nitronaphthylamine is melted with nitrate of potassa. Soluble in alcohol, ether, or glacial acetic acid. Crystallizes in yellow needles; melts at 79°.

*a-Dinitronaphthalene,* $C_{10}H_6(NO_2)_2$, obtained in a similar manner to the above. Difficultly soluble in cold, easily in warm, benzol. From glacial acetic acid it crystallizes in needles, melting at 217°. β-Dinitronaphthalene, isomeric with the above, crystallizes in rhombic plates, melting at 170°.

4. AMINE DERIVATIVES.—The amine derivatives of benzene, toluene, and xylene can be regarded as forming one of the most important groups of raw materials from which are obtained the *basic* coloring matters, all of which contain nitrogen. The structure of the amines can readily be seen if we employ ammonia, $NH_3$, as the type; in this case there are three atoms of hydrogen. If one of these be replaced by an organic radical a *primary amine* is produced; if two, or all three are replaced, a *secondary* or *tertiary amine* respectively is formed.

*Aniline,* or *Amido-benzene,* $C_6H_5.NH_2$.—This substance was discovered by Unverdorben in 1826, who noticed its property of combining with acids to form salts. Runge, subsequently, experimenting upon coal-tar, found a volatile substance which, when treated with a solution of bleaching-powder, produced a blue coloration, giving rise to the name kyanol. It was he who noticed that when a drop of the "nitrate of kyanol" was brought in contact with dried cupric chloride, a black spot was formed. Fritsche, later, examined the distillation products of indigo, and found a body to which he gave the name *aniline.* Aniline was formerly obtained in large quantities by reducing the nitrobenzene with iron filings or scrapings and acetic acid, but now it is wholly produced with hydrochloric acid. The following reaction showing the change that occurs:

$$\underset{\text{(Nitrobenzene.)}}{C_6H_5.NO_2} + 3Fe + 6HCl =$$
$$\underset{\text{(Aniline.)}}{C_6H_5.NH_2} + 3FeCl_2 + 2H_2O.$$

The quantity of acid represented by the above equation is more than sufficient for the purpose, from the fact that ferrous chloride ($FeCl_2$), a reducing agent itself, will act in the reduction of a further quantity of nitrobenzene:

$$C_6H_5.NO_2 + 6FeCl_2 + 6HCl =$$
$$C_6H_5.NH_2 + 3Fe_2Cl_6 + H_2O.$$

Aniline is a liquid, fluid at ordinary temperatures, but when frozen melts at —8°; boils at 182° when pure; specific gravity 1.036; colorless when freshly distilled, but becomes reddish-brown upon exposure to light and air; impurities hasten discoloration. Soluble in alcohol, ether, and benzene in all proportions; in water it is soluble to a slight extent, one hundred parts of water dissolving three parts aniline, while it, in turn, dissolves water to the extent of five per cent.

Aniline forms a series of well-crystallized salts, among which are the *hydrochloride,*—$C_6H_7.N.ClH$,—known as "aniline salt," largely employed in the production of black upon cotton; and the *sulphate,*—$(C_6H_7N)_2H_2SO_4$, of considerable importance.

*Methylaniline,* $C_6H_5.NH(CH_3)$, is obtained by heating aniline hydro-

chloride or a mixture of aniline and hydrochloric acid with rather more than a molecule of methyl alcohol at 200° C. The product is then converted into sulphate and the easily soluble sulphate of methylaniline separated from the sparingly soluble aniline sulphate. The sulphate is decomposed by an alkali and the free base obtained by distillation. The commercial product contains from ninety to ninety-five per cent. of pure methylaniline. It is a colorless oil, boiling at 192° C., and has a specific gravity 0.976 at 15° C.

*Dimethylaniline*, $C_6H_5.N(CH_3)_2$, is obtained by heating a mixture of aniline (seventy-five parts), aniline hydrochloride (twenty-five parts), and methyl alcohol, free from acetone (seventy-five parts), in a cast-iron autoclave at from 230° to 270° C. The product is rectified. The yield is about one hundred and twenty parts from the above proportions. It is a colorless oil, boiling at 192° C., and specific gravity 0.96 at 15° C. Solidifies at +5° C. to a crystalline solid. The commercial product is usually nearly pure.

*Nitraniline*, $C_6H_4(NO_2)NH_2$.—Both the *m*- and the *p*-nitraniline are used technically. The former is made by the partial reduction of dinitrobenzene; the latter from acetanilid, which is nitrated and then freed from the acetyl group by treatment with steam.

*Toluidine*, or *Amido-toluene*, $C_6H_4(CH_3)NH_2$, occurs in three isomers, according to the extent to which the nitration of the toluene was originally carried. *Ortho-toluidine* is produced by the reduction of ortho-nitro-toluene, by the same means as was applied in the case of aniline. It is a fluid, colorless at first, but becoming brown upon exposure. Specific gravity 1.000 at 16°, boiling point 197°; soluble to a slight extent in water (2:100) and in alcohol.

*Meta-toluidine*, occurring similarly to the preceding, is a liquid. Specific gravity .998, boiling at 197°, little soluble in water, but freely in alcohol and ether.

*Para-toluidine* is obtained in the form of large colorless leaflets, crystallizing from alcohol. Specific gravity 1.0017, melting point 45°, and boiling at 198°; slightly soluble in water, readily in alcohol and ether. Commercial toluidine consists chiefly of a mixture of the ortho- and para- bodies, and containing very little aniline; it is of considerable importance in the color industry.

*Xylidine*, or *Amido-xylene*, $C_6H_3(CH_3)_2.NH_2$, homologous with aniline and toluidine, is produced from xylene, as aniline is from benzene,—nitration followed by reduction. Six isomers are obtainable, but the xylidine industrially employed consists of a mixture of five. At ordinary temperature it is a liquid, specific gravity .9184 at 25°, boiling-point 212°. From this derivative the beautiful series of xylidine scarlets are produced.

*Naphthylamine*, $C_{10}H_7.NH_2$.—Two isomers exist. For $\alpha$-Naphthylamine, naphthalene is converted into the nitro- derivative as has been described, and equal parts of this body and water are heated to 80°, incorporated with an equal part of iron filings, and reduced with hydrochloric acid. The product is distilled with lime, and finally rectified by further distillation. Nearly insoluble in water, soluble in alcohol and ether; crystallizes in colorless needles or prisms, which melt at 50° and boil at 300°. Upon contact with the air it acquires a red color, and oxidizing agents cause a blue precipitate to form in solutions of its salts. It finds extensive application in the preparation of several colors of importance. $\beta$-Naphthylamine is produced when

gaseous ammonia combines with β-naphthol in the fused state; commercially it is obtained by the action of ammonio-chloride of calcium, or ammonio-chloride of zinc, upon the same body, assisted by heat, and the subsequent separation of by-products. It occurs in white or pearly leaflets, odorless, difficultly soluble in cold, freely in hot, water, and in alcohol and ether. Melting point 112°, boiling at 294°. Unlike the α-naphthylamine, it is not acted upon by oxidizing agents.

*Phenylenediamine*, $C_6H_4(NH_2)_2$.—Both the *m*- and the *p*- compounds are used in practice. The former is obtained by the reduction of *m*-dinitrobenzene with iron and hydrochloric acid; the latter by the reduction of amidoazobenzene with zinc-dust in aqueous solution.

*Benzidine* (diamido-diphenyl), $\begin{array}{l}C_6H_4.NH_2\\ |\\ C_6H_4.NH_2\end{array}$.—This base is manufactured on a large scale as the basis of the substantive cotton dyes (see p. 418). For its preparation nitrobenzene is reduced by zinc-dust and caustic soda in the presence of alcohol. The hydrazobenzene so obtained is heated in the presence of hydrochloric acid to boiling and the benzidine precipitated from the solution by the addition of sulphuric acid. It forms a grayish-white crystalline solid, fusing at 122° C., and rather difficultly soluble in water.

*Diphenylamine*, $(C_6H_5)_2NH$, is made on a large scale by heating aniline with aniline chlorhydrate in autoclaves to between 220° and 230°. It forms a white or slightly yellowish solid, melting at 54°, and has a pleasant odor of flowers.

5. PHENOL DERIVATIVES.—*Phenol*, $C_6H_5OH$.—The occurrence of this body has been mentioned under tar products, page 359. It crystallizes in needles, which have the well-known odor of "carbolic acid." Specific gravity 1.08, and melting at 37.5°, boiling at 132° to 133°; soluble in water (1 : 15) and readily in alkalies, alcohol, and ether. It finds extensive application in the color and other industries, large quantities being consumed in the manufacture of picric acid.

*Resorcin*, or *Dioxy-benzene*, $C_6H_4(OH)_2$, is obtained from benzene by fusing the sodium sulphonate of the latter with caustic soda. (See page 407.) Occurs in sweetish, colorless crystals, which, however, eventually become dark colored, melting point 110°, boiling-point, 271°; readily soluble in water, alcohol, and ether. Specific gravity 1.28.

*Pyrogallol*, or *Trioxy-benzene*, $C_6H_3(OH)_3$, is readily obtained from gallic or tannic acid when the same are heated to 210° to 220°. It can be obtained from benzene, but the above method is more generally adopted. Processes for its manufacture are detailed on page 408. Pyrogallol occurs in white leaflets, which melt at 115° and boil at 210°; soluble in water, alcohol, and ether.

*Naphthols*, $C_{10}H_7.OH$.—The two derivatives of naphthalene, α- and β-naphthol, find extensive application in the manufacture of artificial coloring matters. They are prepared from the two isomeric naphthalene sulphonic acids, α and β, which are discussed under Processes, page 393. α-Naphthol occurs as lustrous needles, which melt at 94°, boil at 278° to 280°; specific gravity 1.224; sparingly soluble in hot, insoluble in cold, water; soluble in alcohol, ether, benzene, and in solution of caustic alkalies. β-Naphthol occurs in leaflets, melting at 122°, boiling from 285° to 290°; solubility same as for the preceding. Allen (Commercial Organic

Analysis, 2d ed., vol. ii. p. 511) gives the following table of the distinguishing characteristics of the two naphthols:

| α-Naphthol. | β-Naphthol. |
|---|---|
| Crystallizes in small monoclinic needles. | Crystallizes in rhombic laminæ. |
| Melting point 94°; boils at 278° to 280°. | Melting point 122°; boils at 285° to 290°. |
| Faint odor, resembling phenol. | Almost odorless. |
| Volatilizes readily with vapor of water. | Scarcely volatile with vapor of water. |
| Aqueous solution becomes dark violet, changing to reddish-brown on adding solution of bleaching-powder. | Aqueous solution colored pale yellow by solution of bleaching-powder. |
| Aqueous solution becomes red, and then violet, on adding ferric chloride. | Aqueous solution becomes pale green on adding ferric chloride. |

6. Sulpho- Acids.—This group constitutes an interesting and technically valuable series of bodies, which are obtained by the action of concentrated sulphuric acid upon the hydrocarbons, or upon coloring matters already formed.

(1) *Benzene-sulphonic Acid*, $C_6H_5.SO_3H$, is readily obtained by heating two parts benzene with three parts sulphuric acid to 100° C., diluting with water, saturating with carbonate of lead, and decomposing with sulphuric acid to liberate the sulphonic acid. The acid is soluble in water and alcohol, and crystallizes in small plates.

(2) *Benzene-disulphonic Acid*, $C_6H_4(SO_3H)_2$, is produced when benzene is heated with fuming sulphuric acid to 275°. Employed in the production of resorcin.

(3) *Toluene-sulphonic Acid*, $C_6H_4(CH_3)SO_3H$.—No importance.

(4) *Naphthalene-sulphonic Acids*, $C_{10}H_7.SO_3H$.—Two isomeric bodies are obtained when naphthalene is submitted to the action of sulphuric acid. At temperatures ranging from 80° to 100° the α-derivative is largely obtained, and at temperatures from 160° to 170° the β-derivative is produced. Their separation is based upon the different degrees of solubility of the lead salts upon concentrating their aqueous solutions, α-naphthalene sulphonic acid being soluble in twenty-seven parts water, while the β- acid requires one hundred and fifteen parts.

(5) *Anthracene-sulphonic Acid*, $C_{14}H_9.SO_3H$, is produced similarly to the above, or by the reduction of sodium anthraquinone-sulphonate with zinc-dust and ammonia.

*Phenol-sulphonic Acid*, $C_6H_4(OH)SO_3H$.—Three isomers are known, two, the *ortho-* and *para-*, being produced by the direct action of sulphuric acid upon phenol, while the *meta-* compound must be produced by other means. The *ortho-* acid is largely obtained when one part of phenol is slowly mixed with one part of sulphuric acid, care being taken to keep the temperature from rising. The *para-* acid will be obtained if the mixture be heated to 100°. These bodies are much employed as antiseptics under various names; the *para-* compound, also, in the production of picric acid.

*Naphthol-sulphonic Acids*.—The two naphthols are easily converted into mono-sulphonic acids upon being heated to 100° C. with concentrated sulphuric acid; disulphonic acids being produced if the temperature reaches 110° C. *β-naphthol-sulphonic acid*, $C_{10}H_6.SO_3H.OH$. One hundred parts of β-naphthol are added to two hundred parts of sulphuric acid (specific

gravity 1.84) and carefully heated to 50° or 60°, when two acids result, ordinary *β-naphthol-sulphonic acid* (known also as "*Schäffer's acid*," or "*acid S*") and *β-naphthol-α-sulphonic acid* ("*Bayer's acid*," or "*acid B*"). When converted into their sodium salts they can be separated by treatment with alcohol, in which menstruum the latter acid is more soluble than the former. They are extensively used for the production of the croceïn scarlets; and upon nitration yield other colors of importance. If the mixed acid and naphthol is heated to about 20° C. Bayer's acid will be formed, while the employment of a temperature about 90° will cause the formation, as the chief product, of Schäffer's acid.

*Disulphonic Acids of β-Naphthol*, $C_{10}H_5(SO_3H)_2OH$, are obtained when the naphthol is subjected to a temperature of 100° to 110° with three times its weight of sulphuric acid (specific gravity 1.84). Upon dilution milk of lime is added, the precipitated calcium sulphate filtered off, carbonate of soda added, and the whole evaporated to dryness, and lixiviated with alcohol, when "salt G" (yellow shade) is dissolved from "salt R" (red shade). Ordinarily, after the addition of the carbonate of soda, the solution is used without further treatment.

*Anthraquinone-sulphonic Acid*, $C_6H_4(CO)_2C_6H_3.SO_3H$, is formed when anthraquinone is treated with fuming sulphuric acid to 160° C. The unaltered anthraquinone is separated, the solution neutralized with soda, when the white soda salt settles out. The free acid occurs in yellow plates, soluble in water and in alcohol. When fused with either caustic soda or potash *alizarin* is obtained (when the anthraquinone disulphonic acid is used, either by itself or in the melt, *purpurin* is produced along with alizarin); anthraquinone-sulphonic acid being employed directly for the production of this most valuable coloring matter.

*Sulphanilic* (*p-amidobenzene-sulphonic*) *Acid*, $C_6H_4(HSO_3)NH_2$, is made by the action of sulphuric acid upon aniline at about 190° C. Is used very largely as basis of the manufacture of dye-colors.

*Naphthylamine-sulphonic Acids* are prepared from naphthylamine by treatment with sulphuric acid and the application of heat. Several derivatives are produced, which, however, find limited application, mainly in some patented specialties.

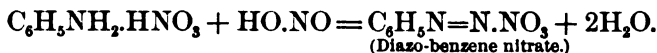
7. Pyridine and Quinoline Bases.—*Pyridine*, $C_5H_5N$, is regarded as a benzene nucleus ($C_6H_6$), with one of the CH groups replaced by an atom of nitrogen. It is obtained when bone oil or other nitrogen-containing organic bodies are distilled. It possesses a pungent odor, is liquid, boils at 116.7°, and is soluble in water; specific gravity .986. A large number of the pyridine derivatives bear a relationship to the alkaloids.

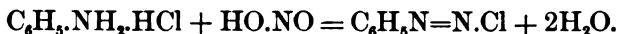
*Quinoline* (*Chinoline*), $C_9H_7N$, differs from pyridine in that naphthalene is the base, $C_{10}H_8$, one nitrogen atom replacing, as before, one of the CH groups. Quinoline is readily prepared by carefully heating in a flask one hundred and twenty grammes glycerine, thirty-eight grammes aniline, twenty-four grammes nitrobenzene (oxidizing agent), with one hundred grammes concentrated sulphuric acid; when the reaction is over, boil for two or three hours, dilute with water, and remove the unchanged nitrobenzene with steam, saturate with caustic alkali, distil, add sulphuric acid and sodium nitrite ($NaNO_2$) to destroy any aniline present, make alkaline, and again distil. Quinoline is a colorless fluid, having a penetrating odor, highly refractive, becoming brown upon exposure to the air; boils at 238°; specific gravity 1.094 at 20°.

*Quinaldine* (*a-Methyl-quinoline*), $C_9H_6(CH_3)N$.—Obtained by the action of hydrochloric acid upon paraldehyde and aniline, for several hours, with the aid of heat. It has a faint odor, is fluid, and boils at 238° to 239°. Technically employed, mainly for the production of "quinoline yellow," cyanine blue, quinoline red, etc.

*Acridine*, $C_{13}H_9N$.—Anthracene is the base from which this derivative is obtained by a substitution of a nitrogen atom for one of the CH groups, as in the previous instances many derivatives of the above bodies exist, which have considerable interest, but no technical importance is attached to them as raw materials.

8. DIAZO- COMPOUNDS.—These form the most extensive, and probably the most thoroughly investigated of the several groups of coal-tar colors. They are produced where nitrous acid (obtained from starch and nitric acid) is allowed to act upon the primary amines of the aromatic series, in which case the following change is noted, assuming aniline nitrate to be acted upon:

$$C_6H_5NH_2.HNO_3 + HO.NO = \underset{\text{(Diazo-benzene nitrate.)}}{C_6H_5N{=}N.NO_3} + 2H_2O.$$

Aniline hydrochloride, treated in the same manner, will yield diazo-benzene chloride:

$$C_6H_5.NH_2.HCl + HO.NO = C_6H_5N{=}N.Cl + 2H_2O.$$

The diazo- compounds differ from those of the *azo-* group in that one of the bonds of the diatomic nitrogen group —N = N— is satisfied with an *hydrocarbon* radicle, while in the latter it is saturated with an atom of oxygen, nitrogen, bromine, chlorine, etc., or with an acid or basic group. The annexed list of diazo- bodies illustrates the above:

| | |
|---|---|
| $C_6H_5N = NCl$ | Diazo-benzene chloride. |
| $(C_6H_5.N = N)_2SO_4$ | " " sulphate. |
| $C_6H_5N = N.Br$ | " " bromide. |
| $C_6H_5N = N.NH.C_6H_5$ | Diazo-amido-benzene. |

The *azo-* compounds have the two nitrogen atoms (—N = N—) united, each to a hydrocarbon group; *mixed azo-* compounds result if these hydrocarbon groups are not identical.

(1) *Diazo-benzene Chloride*, $C_6H_5.N_2Cl$, is formed when nitrite of soda ($NaNO_2$) is added to a solution of aniline chloride in the presence of an excess of hydrochloric acid, the solution being kept cool by means of ice. The product finds application in the manufacture of aniline yellow and other colors.

*Diazo-amido Compounds* result from the action of salts of the diazo-derivatives upon the primary and secondary amines.

*Diazo-amido-benzene*, $C_6H_5.N_2.NH.C_6H_5$, occurs when nitrous acid is passed through a solution of aniline in alcohol; or by adding a solution of sodium nitrite to a mixture of aniline hydrochloride and aniline. Crystallizes in golden-yellow prisms or scales, insoluble in water, easily in ether, benzene, and alcohol; melting point 91°, exploding at a higher temperature.

(2) *Diazo-benzene-sulphonic Acid*, $C_6H_4.N_2.SO_3$ (the anhydride of the sulphonic acid of diazo-benzene).—Sulphanilic acid, $C_6H_4NH_2.SO_3H$ (see p. 402), is dissolved in water, and sodium nitrite added, when the whole is poured into dilute sulphuric acid, which causes a precipitation of the crystals.

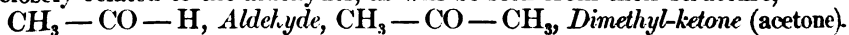
9. Aromatic Acids and Aldehydes.—The *aromatic acids* form a class of bodies of considerable importance, derived from benzenes by substituting the carboxyl group CO.OH for hydrogen. The simplest of the series is *Benzoic Acid* (*Benzene-carboxylic Acid*), $C_6H_5.CO.OH$, which, besides finding extensive application in medicine, is also used in the color manufacture. It can be prepared by a number of methods, chiefly by the sublimation of gum benzoin; by treating the urine of herbivorous animals with hydrochloric acid, which causes the *hippuric acid* to break up, yielding the acid and glycocine; and from *benzyl-chloride* after boiling with nitric acid. It crystallizes in needles or scales, lustrous, and odorless when pure. Specific gravity 1.291, melting at 121°, and boiling at 249°; soluble in alcohol, ether, benzene, etc., sparingly in water.

*Phthalic acid* (*Benzene-dicarboxylic Acid*), $C_6H_4.(CO.OH)_2$.—Three isomers of the above are known, but only the *ortho-* acid will be considered. It is obtained from naphthalene tetrachloride by heating with nitric acid. It can also be obtained by heating naphthalene direct in the presence of nitric acid, but this process is not much employed. It occurs in rhombic crystals, specific gravity 1.585, and melting at 213°; upon being heated, it is liable to split up into water and the anhydride; soluble in hot water, alcohol, and ether. When a phenol is heated with the phthalic anhydride phthaleïns result; of these, the *resorcin* and *pyrogallol-phthaleïns* are the most important, being the basis of the eosins and galleïns and cœruleïns.

*Gallic Acid* (*Trihydroxybenzoic Acid*), $C_6H_2(OH)_3.CO.OH$.—This acid occurs in several vegetable substances,—chiefly gallnuts, sumach, tea, etc. It is ordinarily prepared by heating gallo-tannic acid with dilute mineral acid, or by allowing crushed galls to remain exposed in a moistened state to the action of the atmosphere for some time, when a fermentation takes place, after which boiling with water removes the gallic acid. It yields needle-shaped crystals, sometimes white, but mostly light brown in color. Specific gravity 1.70. When heated to 220° it decomposes, forming *pyrogallol* (Trihydroxybenzene, $C_6H_3(OH)_3$) and $CO_2$. Gallic acid is the chief source of pyrogallol, reference to the application of which has been made under phthalic acid.

*Benzaldehyde* (*Benzoic Aldehyde*), $C_6H_5.CO.H$.—This body, also known as "Bitter Almond Oil," is a colorless liquid, possessing an agreeable odor, and high refracting power. Specific gravity 1.063, boiling at 180°, difficultly soluble in water (1:300), easily in alcohol and ether. Several methods are employed for the production of this substance; for industrial purposes, benzyl-chloride is boiled with nitrate of copper and water, half of the contents are distilled, when the oily layer is separated from the distillate and purified. Mercuric oxide has been used instead of the copper salt. It finds extensive application in the color industry, also for the production of cinnamic and benzoic acid, and several derivatives of value.

10. Ketones and Derivatives, Anthraquinone.—The ketones are closely related to the aldehydes, as will be seen from their structure,—

$CH_3 — CO — H$, *Aldehyde*, $CH_3 — CO — CH_3$, *Dimethyl-ketone* (acetone).

The CO group—carbonyl—is possessed by both classes, but in the aldehydes is united, on the one hand to an alcohol radical, and on the other to an atom of hydrogen. The ketones, however, are distinguished by having two alcohol radicals (alkyls) linked by the CO group.

*Benzophenone*, $C_6H_5.CO.C_6H_5$, is a ketone of the benzene series, and can be obtained by distilling calcium benzoate, or by heating benzoyl chloride

with aluminum chloride and benzene. It occurs in crystals having an aromatic odor, and which melt at 48° to 49°, subliming at 300°. Insoluble in water, soluble in alcohol and ether. It is of some importance, together with the amido- and oxy- derivatives, in the manufacture of certain colors.

*Acetophenone (Phenyl-methyl-ketone)*, $C_6H_5.CO.CH_3$.—This is a mixed ketone, and contains two residues of different hydrocarbons united to the carbonyl group. Acetophenone can be obtained by distilling a mixture of the benzoate and acetate of calcium. It occurs in crystalline plates, melting at 14° to 15°, and boils at 198°.

*Anthraquinone*, $C_6H_4{<}^{CO}_{CO}{>}C_6H_4$.—This substance is of the utmost importance in the manufacture of alizarine. It can be obtained by several processes, the simplest of which is probably the distillation of calcium phthalate, or by oxidizing anthracene ($C_{10}H_8$) with bichromate of potash and sulphuric acid. Anthraquinone is very stable, oxidizing agents having but little effect upon it. When heated it sublimes, yielding yellowish rhombic crystals. Specific gravity 1.425, melting point 273°; insoluble in water, but somewhat in alcohol and ether. Upon fusion with caustic alkalies it yields benzoic acid. For use in the alizarine process, it must first be converted into the sulphonic acid, and this fused with caustic alkali, dissolved in water, and the coloring matter precipitated by a mineral acid, and sublimed. (See Processes of Manufacture, p. 409.)

## II. Processes of Manufacture.

1. Of Nitrobenzene and Aniline.—The commercial production of nitrobenzene is carried out essentially in the following manner, although the details may vary in the different works. Sulphuric acid, 66° Bé., and nitric acid, 42° Bé. (= seventy per cent. $HNO_3$), are mixed together, in the proportion of fifteen parts by weight of the former to ten parts of the latter, in a lead-lined wooden tank (preferably situated above the nitrating apparatus) and allowed to become cold. Three hundred pounds of this "nitrating acid" are run into the nitrating apparatus, either by gravity or by pressure, when the benzene is allowed to flow in in a slow, steady stream. During the admission of the benzene the temperature, which should be maintained between 80° C. and 90° C., is regulated by means of water kept at about 50° C. circulating around the vessel, or stopping the inflow, should the temperature give indication of rising, thereby producing the dinitro- derivative. About one hundred pounds of benzene are used, although this quantity is subject to change, according to quality. After the nitration is finished, the contents of the vessel are emptied slowly into large tanks, the acid layer being drawn off first, and the nitric acid recovered therefrom, and the nitrobenzene, insoluble in the acid, coming last, is immediately poured into a tank containing water, and washed, followed by a wash with caustic alkali, and finally agitated with water.

The quantities by weight of the two acids to effectually nitrate either benzene, toluene, or xylene, is shown below:

| | | | |
|---|---|---|---|
| 100 kilos. | benzene . . . . . | 120 kilos. nitric acid. | 180 kilos. sulphuric acid. |
| 100 " | toluene . . . . . | 105 " " " | 175 " " " |
| 100 " | xylene . . . . . | 90 " " " | 150 " " " |

Or, of a standard mixture of one hundred kilos. nitric acid and one hundred and fifty kilos. sulphuric acid, there will be required for the effectual nitration of one hundred kilos. of the above tabulated hydrocarbons three hundred, two hundred and sixty, and two hundred and twenty-five kilos. respectively. The form of nitrating apparatus in use is usually cylindrical, with a flat or round bottom. Fig. 113 illustrates the latter form. The cover is provided with several openings: *f* is for general charging; *e* is for the gas exit, while provision is made for the introduction of the thermometer, and for carrying the agitator shaft. The opening for withdrawing the charge is at *g*. The best plan in arranging the plant is to provide for the acid mixing and nitrating on one floor, on the floor below the washing, and, if desirable, a steam still employed to separate the benzene which has not been acted on by the acids, and which is always found dissolved in the nitrobenzene. On the lowest floor, the alkali and final water-wash. If all the operations are performed on one level, a "monte-jus" should be used for the transportation of liquids.

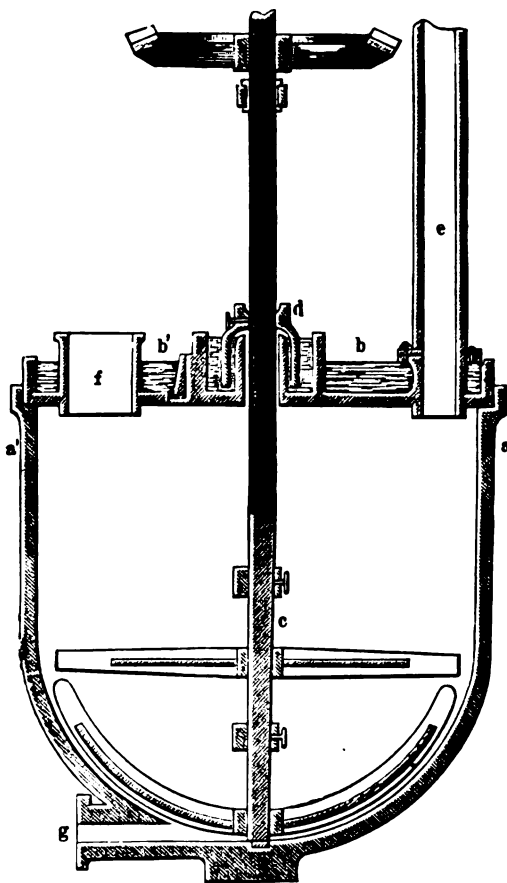
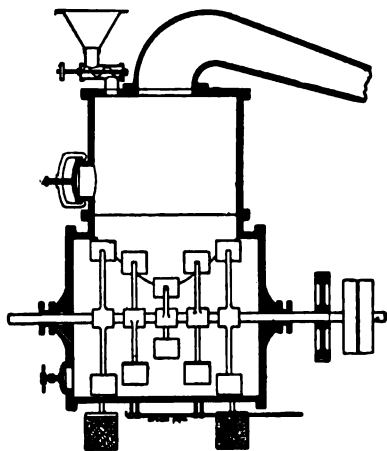



Fig. 113.

*Aniline* ("Aniline Oil" of commerce).—Aniline is obtained by the treatment of nitrobenzene with iron filings or scrapings and hydrochloric acid. The apparatus employed are generally of two kinds, vertical and horizontal, the method of working being in each case the same. In the former, the agitator is attached to an upright hollow shaft, so constructed as to provide for the admission of steam to the bottom of the vessel. The cover supports the gearing, and gooseneck for leading the vapors to the condenser, etc. The horizontal form is shown in Fig. 114; the construction provides for agitators attached to a horizontal revolving shaft passing through boxes in the heads. Steam enters through the pipes underneath. A steady supply of fine iron is maintained by means of the mechanical feed on the cover. The operation is conducted by adding some of the iron filings with water, followed by the acid and nitrobenzene; steam is turned on, and, the agitators set in motion, at once the reaction begins, and a mixture of nitroben-

zene, aniline, and water appears in the condenser, which is continually returned to the main body in the apparatus; after the reaction has commenced and the distillate comes over regularly, the iron can be fed steadily, or at uniform intervals. If all the iron is added at once, serious loss is occasioned by a reduction of aniline to benzene and ammonia. For a charge of six hundred kilos. of nitrobenzene, about seven hundred kilos. of iron filings will be required and sixty kilos. of 21° Bé. hydrochloric acid. The solubility of the distillate in hydrochloric acid is noted, until a point is reached at which no nitrobenzene separates in an unaltered condition. Formerly it was the general practice to add lime to the tank, and distil off the aniline by means of steam; now the contents are emptied into large tanks containing water and allowed to subside for a day or more, when the lower layer, consisting of aniline, is drawn off and pumped into a large iron still mounted over an open fire and rectified. One hundred parts of nitrobenzene will yield about seventy-five parts of aniline if the process is carefully attended. Ordinarily, the yield will be from seventy-one to seventy-four parts.

Fig. 114.

2. Of Phenols, Naphthols, etc.—*Phenol.*—See Chapter XI., "Coal-tar Distillation," p. 377.

*Resorcin* is manufactured commercially from the soda salt of benzene-disulphonic acid, by fusing with caustic soda and subsequent extraction with ether. One hundred kilos. of fuming sulphuric acid are contained in a large cast-iron vessel provided with means for agitating the contents, and into it is gradually allowed to flow twenty-eight kilos. of benzene; the whole is maintained at a moderate temperature for several hours, and finally raised to about 270° C. to 275° C., after which the contents are transferred to a large volume of water and boiled. Lime is added, the precipitated sulphate removed, and the soluble lime salt decomposed by the addition of the requisite quantity of carbonate of soda; carbonate of lime is precipitated, filtered, and the precipitate freed from the excess of solution in the filter-press. This solution is evaporated to dryness in iron pans. For the resorcin melt, sixty kilos. of the above salt and one hundred and fifty kilos. of 76° caustic soda are fused together for about eight hours at a temperature near 270°; when fusion is finished the melt is cooled, leached out with boiling water, and boiled with hydrochloric acid for some time, when the heat is withdrawn, and the solution allowed to become cold, and subjected to the action of ether or benzene in an extraction apparatus, which removes the resorcin. The benzene is distilled off and recovered, while the crude resorcin remaining is dried at about 210°. Pure resorcin is obtained from the above by distillation.

*Pyrogallol.*—Several processes are employed for the production of this substance, all being based upon the use of an aqueous extract of gallnuts or of gallic acid. One process is carried out by heating a glycerine solu-

tion of gallic acid to about 200° C., diluting with an equal volume of water, and extracting therefrom the pyrogallol with ether, which is evaporated off and recovered. Another process is to heat one part of gallic acid and two parts water in a closed vessel to 200° to 210° C. for half an hour, cooled, and heated with bone-black, the solution filtered, and evaporated to the crystallizing-point. The crystals are further purified by being distilled in a vacuum.

*Alpha- and Beta-Naphthols.—α-Naphthol* is manufactured on a large scale in the same general manner as resorcin. α-Naphthalene-sulphonic acid is first prepared by heating naphthalene with fuming sulphuric acid to 90° C., diluting with water, and completely neutralizing with milk of lime, filtering from the magma of sulphate which is passed through a filter-press, the solution of the soluble lime salt decomposed with carbonate of soda, filtered and pressed again, and the solutions finally evaporated to crystallization, when, on cooling, the β-naphthalene-sulphonate separates out and is removed. The α- salt is fused with caustic soda, when the corresponding naphthol is obtained.

*β-Naphthol*, of much more commercial importance than the preceding, is manufactured similarly. The naphthalene-sulphonic acid is made as above, but at a temperature of 200° C., in order to obtain a large yield of the β- derivative. This is converted into the soda salt, dried, and one part by weight fused with two parts of caustic soda dissolved in the smallest quantity of water, at a temperature of 270° to 300° C.; when the reaction is over, the melt is treated with water, the β-naphthol separated by the addition of hydrochloric acid, filtered, dried, melted, and poured into cylindrical moulds.

3. Of Aromatic Acids and Phthaleïns.—*Benzoic Acid* can be manufactured by several processes and from different sources. For technical purposes the manufacture from benzoin resin and from hippuric acid need not be considered, as it is made almost exclusively on a large scale from the chlorine derivatives of toluene, such as benzal chloride, $C_6H_5.CHCl_2$, and benzo-trichloride, $C_6H_5CCl_3$. The former, when heated with water or milk of lime under pressure, is changed into benzaldehyde, $C_6H_5CHO$, which, however, always has some benzoic acid formed with it as a side-product. The benzo-trichloride, similarly with water or milk of lime, yields benzoic acid according to the reaction $C_6H_5.CCl_3 + 2H_2O = C_6H_5.COOH + 3HCl$. The benzoic acid so obtained is almost always contaminated by some chlor-benzoic acid.

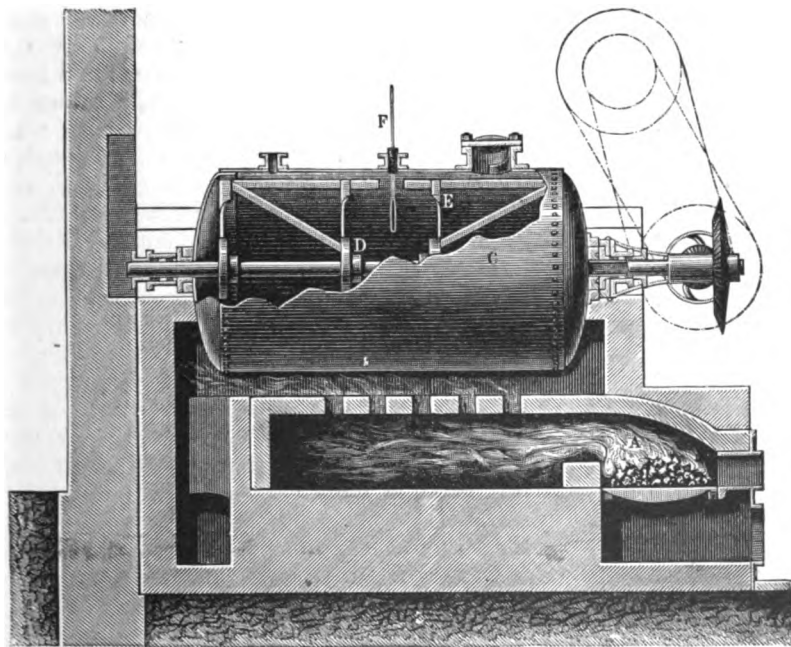
*Phthalic Acid and Phthalic Anhydride.*—The process for their manufacture is as follows. Naphthalene is converted into the tetrachloride derivative by means of chlorine gas acting upon it in the fused state, or by grinding naphthalene with an alkaline chlorate and sufficient moisture to cause the mass to cohere, when it is dried in small lumps, which are immersed in concentrated hydrochloric acid, when the tetrachloride separates as a sticky mass, afterwards becoming hard. This is taken and acted upon by concentrated nitric acid, heated till the solution is complete and the excess of nitric acid has been distilled off, when, upon cooling, the phthalic acid separates out in crystals. The *anhydride* is obtained by acting upon phthalic acid, heated to about 200° C., with carbon dioxide and subliming.

*Phthaleïns.*—When phthalic acid or its anhydride acts upon phenols a class of bodies termed "phthaleïns" are formed with elimination of water. *Phenolphthaleïn* is manufactured by heating the anhydride, phenol, and sulphuric acid for ten to twelve hours at 120° C.; the sulphuric acid acts only as a dehydrating agent. The melt is boiled with water, the residue dis-

solved in caustic soda, and the phthaleïn is precipitated upon the addition of an acid. *Resorcin-phthaleïn*, or *Fluoresceïn*, is obtained by heating three parts of phthalic anhydride with about four parts of resorcin until the fusion yields no more vapors, and becomes solid at a temperature not exceeding 210° C. The melt is dissolved in dilute caustic soda, with an addition of phosphate of soda and chloride of calcium to remove impurities. The fluoresceïn is precipitated from the solution by the addition of dilute hydrochloric acid.

4. OF ANTHRAQUINONES, ETC.—Anthracene in a finely-divided state is suspended in water by agitation, and oxidized by means of potassium bichromate and sulphuric acid at a boiling temperature; allowed to cool, and the anthraquinone is collected on filter-frames, washed with water and dried, and for further purification is treated with concentrated sulphuric acid, and heated to 110° to 120° C., when the dark mass obtained is treated with steam, which causes a dilution, followed by a gradual separation of the anthraquinone in crystals. These are washed with hot water, and afterwards with hot dilute soda to remove organic acids. The yield is about fifty to fifty-five per cent. of the weight of the anthracene used.

*Anthraquinone-monosulphonic Acid.* (See p. 402.)—This is manufactured by heating one hundred kilos. anthraquinone with one hundred kilos.

FIG. 115.

fuming sulphuric acid (containing forty-five to fifty per cent. anhydride) to 160° C. in an enamelled cast-iron vessel mounted in an oil-bath. By varying either the quantity of sulphuric acid or the temperature the alpha- or beta-disulphonic acid will result. The separation of the two latter from the mono-sulphonic acid is effected by converting the sulphonic acids into lead salts, decomposing these with carbonate of soda, and acting upon the

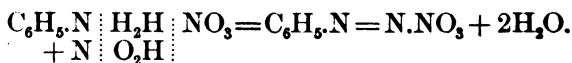
resulting soda salts with dilute sulphuric acid, which has but a slight solvent action upon the mono-sulphonic acid.

*Alizarin.*—The alizarin process is carried on in large iron vessels or autoclaves, mounted as shown in Fig. 115. To the central shaft *D* agitators are attached, so that the charge may be constantly mixed. *F* is a thermometer, and the openings in the top to the right are for introducing the charge, and the small one on the left for admitting steam and water. The process is commenced by melting two hundred and fifty to three hundred parts of caustic soda in a small quantity of water, and then adding twelve to fifteen parts of chlorate of potash and one hundred parts of the sodium anthraquinone-sulphonate, when the vessel is closed and the agitator put in motion, the whole being kept at a temperature of 180° C. for two days, when it is allowed to cool, dissolved in a large quantity of water, and the alizarin precipitated by the addition of hydrochloric acid. The alizarin is washed to free it from soda salts, passed through filter-presses, and is ready to be either dried and ground, or ground in glycerine to a paste. Neutralizing the soda solution with sulphurous acid instead of with hydrochloric acid enables a recovery of the caustic soda. The yield from one hundred kilos. anthraquinone is one hundred and five to one hundred and ten kilos. alizarine (Schultz). Several processes are employed, varying mainly in the duration of the melt and in the proportion of materials used. Instead of soda, lime is employed, in which case a "lake" is formed.

5. OF QUINOLINE (CHINOLINE) AND ACRIDINE.—Quinoline is produced from nitrobenzene and aniline. Twenty-four grammes of the former and thirty-eight grammes of the latter, with one hundred and twenty grammes of glycerine, are placed in a flask (provided with a return condenser) containing one hundred grammes of concentrated sulphuric acid; when the reaction is over, the contents are boiled for some time, diluted, and the unconsumed nitrobenzene is distilled off; an excess of alkali is added to the solution, and the quinoline distilled off with a current of steam. It can also be obtained from crude quinoline from coal-tar with phthalic anhydride and zinc chloride. *Acridine* is found along with crude anthracene, from which it is separated by treatment with dilute sulphuric acid, precipitating with chromate of potash, recrystallizing, precipitating by ammonia, dissolving in hot water, from which it separates in crystals on cooling.

6. SULPHONATING.—This general process consists in dissolving the compound to be changed in fuming sulphuric acid, whereby one or more H atoms are replaced by $HSO_3$ groups, producing mono-, di-, or trisulphonic acids. Examples of this process are given under Resorcin (see p. 407), the Naphthols (see p. 408), and will frequently be referred to in classifying the artificial dye-colors.

7. DIAZOTIZING.—By the action of nitrous acid upon primary aromatic amines a diazo- compound is formed, as in the following reaction:

$$\begin{array}{l} C_6H_5.N \,\vdots\, H_2H \,\vdots\, NO_3 = C_6H_5.N = N.NO_3 + 2H_2O. \\ \quad\;\; + N \,\vdots\, O_2H \,\vdots \end{array}$$

These diazo- compounds are susceptible of a great variety of reactions whereby other groups or atoms of elements may be substituted. Thus, by the aid of the diazotizing reaction it is possible to replace a $NO_2$ or a $NH_2$ group by OH, H, Cl, Br, I, CN, etc. It is therefore of the greatest importance in synthetic organic chemistry.

The process is carried out in one of two general ways: (*a*) by conducting a current of nitrous acid gas through a solution of the substance to be diazotized, the nitrous acid in this case being most conveniently obtained by acting upon starch with concentrated nitric acid in a suitable generator, or (*b*) by diazotizing in a bath together with the nitrous acid-yielding substance (nitrite of soda generally). In this case the gas is evolved by adding an acid, usually sulphuric, to the solution. Diazotizing is always conducted at a low temperature.

## III. Products.

It would be impossible in the space of this chapter to do more than give a classification of the artificial dye-colors and enumerate a few of the more important under each group. The number of distinct products has already run far into the thousands, and the trade-names by which many are exclusively known frequently bear so little relation to the chemical names that it would be idle for us to attempt to cover the ground in any other way than by a simple outlining at present. But before taking up this classification it will be well to examine what general principles, if any, underlie the production of a dye-color. O. N. Witt* has proposed a theory which explains in a very simple way this color formation in the aromatic series. He names a series of radicals or groups which by their entrance alone or with others change a colorless hydrocarbon into a colored compound. These radicals, which he calls "chromophor" groups, are only capable of producing the "chromogens," or parent substances of dye-colors, which chromogens, however, are at once changed into dye-colors of distinct basic or acid character when a salt-forming group enters. Thus, from two molecules of benzene by the entrance of the chromphor group —N=N— is formed *azo-benzene*, an orange-colored chromogen, but not capable of dyeing silk or wool. When the $NH_2$ group enters there results, however, *amido-azo-benzene*, a real dyestuff. Or from benzene by the entrance of the chromophor group $NO_2$ is formed the chromogen trinitro-benzene, which by the entrance of the salt-forming group OH becomes trinitro-phenol (or picric acid), a yellow dye-color.

Witt indicates some eleven of these chromophor groups, to which we shall refer under the appropriate heads in our classification. Of salt-forming groups which change the chromogens to dyestuffs, two are specially to be noted, the amido group $NH_2$, which imparts a basic character to the dye-color, and the hydroxyl group OH, which gives the dye-color an acid character. Almost all dye-colors are changed to colorless compounds by the action of reducing agents. The nitro- compounds are changed into the corresponding amido- derivatives, the azo- compounds into hydrazo- or even amido- compounds, while more complex dye-colors are changed by careful reduction into bodies richer in hydrogen, which are known as "leuco" compounds. From these "leuco" compounds the corresponding dye-colors are then formed more or less easily by oxidation. In some cases atmospheric oxidation alone suffices, as with indigo, in others more energetic oxidizing agents, such as lead peroxide, are needed.

Again, the study of dye-colors soon shows that they possess different characters with reference to the ease with which they may be fastened upon

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* Berichte der Chem. Ges., ix. p. 522.

the fibre to be dyed or the kind of mordant needed to effect such fastening upon the fibre. We therefore distinguish between basic, acid, and indifferent or neutral dyestuffs. Basic dyes like magenta fasten upon the animal fibre at once, and upon the vegetable fibres after treatment with tannic acid and similar acid mordants. They are used in the form of their salts. The acid dyes are frequently sparingly soluble, and are either brought into soluble condition by forming alkaline salts and sulphonic derivatives, which are then used for dyeing, or they are used with fibres previously mordanted with metallic hydrates or salts, as in the case of alizarin. In the latter case, however, the color acid forms a variety of different colored compounds (lakes) with the different bases. To the third class (indifferent or neutral bodies) belongs indigo-blue and some other substances.

The classification which is now generally accepted is that based in the main upon Witt's chromophor groups, and we will simply note a few illustrative compounds under each group.

1. ANILINE OR AMINE DYE-COLORS.

(*a*) TRIPHENYL-METHANE DYES (Chromophor group, —C= ⎣—N).—*Benzaldehyde Green* (or Malachite Green), known also under a variety of other names, is made by the action of benzaldehyde upon dimethyl-aniline. The commercial dye is the oxalate or zinc chloride double salt.

*Brilliant Green* (or Solid Green) is the corresponding derivative from diethyl-aniline. The sulphate or zinc chloride salt is used as dye.

*Magenta* (Aniline Red, or Fuchsine) is a mixture of the chlorhydrates of para rosaniline and rosaniline, and is obtained by oxidizing aniline oil with arsenic acid or nitrobenzene. A large number of side-products are obtained in the manufacture of magenta, and have been used under the names of cerise, cardinal, amaranth, chrysaniline, phosphine, maroon, mauvaniline, etc.

*Acid Magenta* (Fuchsine S) is the sodium or ammonium salt of pararosaniline and rosaniline trisulphonic acids, and is prepared by sulphonating the ordinary magenta.

*Aniline Blue* (spirit soluble Blue) is a salt of triphenylated para-rosaniline, and is made by the action of a large excess of aniline upon rosaniline. If magenta is used instead of rosaniline a reddish-blue is obtained.

*Diphenylamine Blue* (spirit soluble) is probably the chlorhydrate of triphenylated para-rosaniline, and is made, as the name indicates, from diphenylamine, which is heated with oxalic acid to 120° to 130° C.

*Alkali Blue* (Nicholson's Blue, Soluble Blue) is the sodium salt of the monosulphonic acid of a spirit soluble blue, and is made by sulphonating the latter.

*Höchst New Blue* is the calcium salt of the di- or tri-sulphonic acid of trimethyl-triphenyl-pararosaniline.

*Hofmann's Violets* consist of salts of the ethyl and methyl derivatives of rosaniline and pararosaniline, and are made by the action of methyl or ethyl chloride or iodide upon magenta in the presence of caustic soda. It is of historic interest, but has been replaced almost completely by methyl violet.

*Methyl Violet* is a salt of pentamethyl pararosaniline, and is produced by the direct oxidation of the purest dimethylaniline with copper chloride.

*Acid Violet* is obtained by condensing dimethyl-*p*-amido-benzaldehyde with ethyl-benzylaniline-sulphonic acid, and oxidation of the product.

*Methyl Green.*—This dye is formed by the action of methyl chloride upon methyl violet. The commercial dye is the zinc double chloride.

(*b*) Diphenyl-methane Dyes.—*Auramine*, an important yellow dye, is prepared by the action of phosgene gas, $COCl_2$, upon dimethylaniline and heating the product with sal ammoniac and zinc chloride to from 150° to 160° C.

*Pyronine* is a red dye obtained by condensing formaldehyde with dimethyl-*m*-amidophenol and oxidizing the product.

(*c*) Azines (Eurhodines and Safranines).—Chromophor group =N—N=. *Neutral Red* (Toluylen Red) is a basic dye-color prepared by the action of nitroso-dimethyl-aniline upon *m*-toluylen-diamine. It is used with cotton after mordanting with tannic acid and tartar emetic.

*Safranine* (Aniline Rose) is prepared by the oxidation of amidoazotoluene and toluidine, or of *p*-toluylen-diamine, ortho-toluidine, and aniline. The commercial salt is the chlorhydrate of the safranine base.

*Naphthalene Red* (Magdala Red) is the compound in the naphthalene series corresponding to the preceding. It is obtained by fusing the chlorhydrate of α-naphthylen-diamine, α-naphthylamine, and amidoazonaphthalene. It forms a dark-brown powder, soluble in alcohol with strong red fluorescence. It is used largely in silk-dyeing and for velvet because of its fine color and fluorescence.

*Mauveïn* (Perkin's Violet) is of historic interest mainly as the first aniline color. It was obtained by W. H. Perkin in 1856 by the oxidation with sulphuric acid and bichromate of potash of a mixture of aniline and toluidine.

*Methylene Violet* is a reddish-violet dye obtained by the action of hydrochloride of nitrosodimethylaniline upon a mixture of the hydrochlorides of *m*- and *p*-xylidine.

*Indoines* are basic coloring matters dyeing cotton deep shades from dark violet to indigo-blue, fairly fast to light and washing. They are made by combining diazotized safranines with α- and β-naphthol and conversion into hydrochlorides.

(*d*) Indulines and Nigrosine.—*Induline, spirit soluble* (Coupier's Blue, Guernsey Blue, etc.) is prepared by heating amidoazobenzene with aniline to 160° C.

*Induline, water soluble* (Indigo substitute), is the sodium salt of the disulphonate of the preceding, and is extensively used for silk and wool.

*Nigrosine* is prepared by heating nitrophenol with aniline and aniline chlorhydrate. The alcohol soluble compound is the simple salt of the base, while the sodium sulphonate forms the water soluble compound.

*Paraphenylene Blue* is a dark blue dye of the induline class obtained by the action of *p*-phenylene-diamine upon hydrochloride of amidoazobenzene.

*Naphthyl Blue* is the sodium sulphonate of anilido-phenyl-naphthinduline. Dyes silk blue with a red fluorescence, and is faster to light than the ordinary indulines.

(*e*) Aniline Black.—For the preparation of aniline black, aniline chlorhydrate is very carefully oxidized. The dyestuff is not prepared for dyeing or printing, but is fixed on the fibre by an oxidation process which develops it gradually. It is a very fast black. Quite a variety of oxidizing agents may be used. Potassium chlorate and copper sulphate are frequently used in admixture, and vanadate of ammonia is also of especial serviceableness in connection with the chlorate. Electrolysis of a concentrated solution of an aniline salt will also produce aniline black.

2. Phenol Dye-colors.

(*a*) Nitro-Derivatives.—*Picric Acid* (Trinitrophenol) is made by nitrating carbolic acid direct with strong nitric acid, or, better, by acting upon phenol-sulphonic acid with strong nitric acid. Forms light yellow leaflets or scales, and is extensively used as a dye for silk and wool.

*Naphthol Yellow* (Martius Yellow, Manchester Yellow, etc.) is the sodium, potassium, or calcium salt of dinitro-α-naphthol, and is prepared by the nitration of α-naphthol either directly, or after conversion into the monosulphonic acid.

*Naphthol Yellow S* is a sulphonate of the preceding, and is made by nitrating the α-naphthol-trisulphonic acid. The color is faster than picric acid or the simple naphthol yellow.

*Aurantia* is the ammonium salt of hexa-nitro-diphenylamine, and is made by the nitration of diphenylamine. It was formerly used for wool and silk, but is now used only for leather coloring.

(*b*) Rosolic Acids.—*Rosolic Acid* and *Aurin* (Pararosolic Acid) may be prepared from rosaniline and pararosaniline respectively by treatment with sodium nitrite and after boiling in the presence of sulphuric acid. These two coloring matters are no longer of commercial importance.

*Yellow Corallin* is prepared by heating pure phenol with concentrated sulphuric acid and oxalic acid for some hours until the evolution of gas nearly ceases. The crude product of the reaction obtained by pouring the melted mass into water is changed into the commercial dye by dissolving it in caustic soda solution and evaporation to dryness.

*Red Corallin* (Paëonin) is obtained by the action of ammonia under pressure upon the yellow corallin, and represents an intermediate product between aurin and para-rosaniline.

(*c*) Phthaleins.—*Phenol-phthalëin* is not used as a dyestuff, but as an indicator in alkalimetry.

*Fluorescëin* (Resorcin Phthalëin) is made by heating molecular proportions of resorcin and phthalic anhydride to 195° to 200°. Fluorescëin is not used as such for dyeing, but is converted into the eosins. The sodium salt of the fluorescëin comes into commerce under the name of uranine.

*Eosins.*—The several halogen substitution derivatives of fluorescëin form the class of dyes known as *eosins.* Thus, the potassium or sodium salt of tetrabrom-fluorescëin is the *eosin yellow shade,* while the corresponding salts of tetraiodo-fluorescëin constitute *eosin blue shade. Methyl* and *Ethyl Eosin* (Primrose) are the methyl and ethyl ethers of tetrabrom-fluorescëin. *Aureosin* is a chlorinated fluorescëin. *Saffrosine* is the potassium or sodium salt of dibrom-dinitrofluorescëin. *Erythrosin* is the potassium salt of di-iodo-fluorescëin. *Rose Bengale* is the sodium salt of tetraiododichlor-fluorescëin. *Phloxin* is the potassium salt of tetrabromdichlor-fluorescëin, and *Cyanosine* is the potassium salt of the methyl ether of phloxin. *Rhodamine* is the phthalëin of diethyl-meta-amidophenol. *Cyclamine* is obtained by the action of iodine upon thionated dichlor-fluorescëin. *Violamine* is obtained by the action of *o*-toluidine upon fluorescëin chloride and sulphonation of the product. Wool and silk especially are dyed with the eosins, and cotton after mordanting with various metallic salts.

*Gallëin* is the phthalëin of pyrogallol, and is prepared by an analogous method to that described under fluorescëin. It is very little used in dyeing, but serves for the preparation of

*Cœrulëin.*—This dye is obtained by heating gallëin with twenty times its weight of strong sulphuric acid. Forms a dark amorphous mass, which dissolves in alkalies with a beautiful green color. Cœrulëin forms a colorless compound with sodium bisulphite, which is known as *Cœrulëin S*, and is much used in dyeing, as it is easily decomposed by steaming.

3. Nitroso and Oxyazine Colors.

(*a*) Nitroso Colors (Chromophor group $= N - OH$).—*Gambine* is obtained by the action of nitrous acid upon $\alpha$-naphthol. It dyes iron-mordanted fabrics green.

*Dinitrosoresorcin* is obtained by the action of nitrous acid upon resorcin. Dyes like the previous color.

*Dioxine* is obtained by the action of nitrous acid upon dioxynaphthalene. Dyes bright green or brown shades on metallic mordants.

(*b*) Indophenols and Indamine (Chromophor, $N = O$, ring-closed).—*Indophenol* ($\alpha$-Naphthol Blue) is prepared by oxidizing dimethyl-paraphenylene-diamine and $\alpha$-naphthol with bichromate of potash and acetic acid. Indophenol may be reduced by glucose and caustic soda to a leuco- compound known as *Indophenol white*, which is also sold commercially. When cotton goods are printed with leuco-indophenol, the blue color may be developed in dilute bichromate of potash solution.

*Indamines* are obtained by heating the indulines with *p*-phenylene-diamine and *p*-phenylene-diamine hydrochloride. Dyes deep indigo-blue shades on cotton mordanted with tannin and tartar emetic.

(*c*) Oxyazines (Chromophor $\langle {}^{-N}_{O} \rangle$).—*Azurine* is obtained by the action of nitrosodimethyl-aniline hydrochloride upon *sym*-dioxybenzoic acid. Dyes a violet blue on chrome-mordanted wool or cotton.

*Gallocyanine* is obtained by the action of nitrosodimethyl-aniline upon gallic acid. It is a gray paste, insoluble in water, but soluble in alcohol with bluish-violet color.

*Prune Pure* is the methyl-ether of gallocyanine.

*Gallanilic Indigo* is the sodium bisulphite compound of gallocyanine-anhydride-anilide.

*Meldola's Blue* is obtained by the action of nitrosodimethyl-aniline hydrochloride upon $\beta$-naphthol. Dyes cotton mordanted with tannin and tartar emetic indigo-blue.

*Nile Blue, Capri Blue,* and *Gallamine Blue* are all oxyazine colors obtained by analogous reactions of nitrosodimethyl-aniline or the corresponding amidophenol.

*Resorcin Blue.*—By the action of nitrous acid upon resorcin is produced diazoresorcin, which by the action of concentrated sulphuric acid is changed into diazoresorufin. This yields a hexabrom- derivative, the ammonium salt of which is the commercial dye. It is used for dyeing silk and wool a blue color, which has a red fluorescence, especially by artificial light. By combining with yellow dyes it yields a fluorescent olive color.

(*d*) Thiazines (Chromophor $\langle {}^{-N}_{S} \rangle$).—*Methylene Blue* is prepared from dimethyl-aniline by the treatment of this first with sodium nitrite and then with hydrogen sulphide after acidifying with hydrochloric acid. The

commercial salt is a zinc double chloride of the sulphur base, called tetramethyl-thionin.

4. AZO DYE-COLORS.—Chromophor group, —N = N—.

A. MONOAZO DYES.—(*a*) *Amidoazo Dyes.*

*Chrysoidine* (Diamidoazobenzene Hydrochloride) is obtained by admixing solutions of diazobenzene hydrochloride and *m*-phenylene-diamine. Forms reddish-brown crystals.

*Phenylene Brown* (Bismarck Brown, or Vesuvine) is triamido-azobenzene hydrochloride. Forms a brown powder soluble in water.

*Butter Yellow* is dimethylamidoazobenzene. This yellow dye is soluble in oils and is much employed for coloring butter, oils, etc.

*Acid Yellow* (Fast Yellow) is the sodium salt of the disulphonic acid of aniline yellow (amidoazobenzene). It is used largely in dyeing compound shades.

*Dimethyl-aniline Orange* (Helianthin) is the ammonia salt of dimethyl-aniline-azobenzene-sulphonic acid. Dyes silk and wool a fiery orange. It is also used as an indicator in alkalimetry, as the light yellow color of the solution is immediately turned red by the addition of a drop of hydrochloric acid.

*Diphenylamine Orange* (Tropæolin OO, Orange IV) is formed by the action of diazobenzene-sulphonic acid upon diphenylamine. Dyes silk or wool a very fine golden yellow.

*Metanil Yellow* is the sodium salt of phenylamidoazobenzene-*m*-sulphonic acid. Forms a yellow soluble powder.

*Archil substitute* (naphthion red) is made by combining *p*-nitraniline with naphthionic acid or *β*-naphthylamine-sulphonic acid.

(*b*) *Oxyazo Dyes.*—*Soudan G* (Aniline-azoresorcin) is a brown powder hardly soluble in water, soluble in alcohol. It is used for coloring spirit varnishes, oils, etc.

*Soudan Brown* (Pigment Brown) is made by the action of hydrochloride of *α*-diazonaphthalene upon *α*-naphthol. It is used for coloring varnishes, soaps.

*Carmine-naphte* is an isomeric compound formed from *β*-diazonaphthalene and *β*-naphthol. Forms a red-brown powder, soluble in sulphuric acid with fuchsine-red color.

*Alizarin Yellow* is a yellowish-brown dye made by combining *p*-nitraniline with salicylic acid.

*Fast Brown N* (Naphthylamine Brown) is made by combining naphthionic acid with *α*-naphthol. Dyes wool brown from an acid bath.

*Crocëin Orange* (Ponceau 4GB) is prepared from hydrochloride of diazobenzene and *β*-naphthol-monosulphonic acid. It is a fiery-red powder, dyeing a reddish orange on wool.

*Orange G* is the sodium salt of diazobenzene-*β*-naphthol-disulphonic acid. It dyes an orange-yellow shade.

*Cochineal Scarlet 2R* results from the action of diazotoluene upon *α*-naphthol-monosulphonic acid. It forms a cinnabar-red dye-color.

*Azococcin 2R* results from the action of hydrochloride of diazoxylene upon *α*-naphthol-sulphonic acid. It forms a red-brown powder, difficultly soluble in water. It is used in silk dyeing.

*Wool Scarlet R* results from the action of hydrochloride of diazoxylene upon *α*-naphthol-disulphonic acid. It forms a brown-red powder, soluble in water with yellowish-red color.

*Ponceau 2R* (Xylidine Red) results from the action of hydrochloride of diazo-*m*-xylene upon β-naphthol-disulphonic acid. It forms a red powder, easily soluble. It has been used in large quantities as a substitute for cochineal.

*Ponceau 3R* (Cumidine Red) results from the action of hydrochloride of diazo-*m*-cumene upon β-naphthol-disulphonic acid. It is used as the preceding, but gives redder shades.

*Anisol Red* and *Phenetol Red* are formed by the action of anisidine and amido-phenetol respectively upon β-naphthol-disulphonic acid.

*Fast Red B* (Bordeaux B) is formed by the action of hydrochloride of diazonaphthalene upon β-naphthol-disulphonic acid.

*α-Naphthol Orange* (Tropæolin OOO, No. 1) is the sodium salt of *p*-sulphanilic-acid-azo-α-naphthol. Forms orange-yellow scales, tolerably soluble in water. It dyes silk and wool a reddish orange.

*β-Naphthol Orange* (Tropæolin OOO, No. 2, Mandarin) results from the action of *p*-diazobenzene-sulphonic acid upon β-naphthol in alkaline solution. It forms an orange-red soluble powder, and is used largely for wool-dyeing.

*Fast Red A* (Rocelline, Cerasine, etc.) is prepared by uniting α-diazonaphthalene-sulphonic acid acid with β-naphthol. It forms a brown-red powder, more soluble in hot than in cold water. It is used largely as a substitute for barwood and orseille.

*Azorubin S* (Fast Red C, Carmoisin) is the sodium salt of the disulphonic acid of naphthalene-azo-α-naphthol. It forms a reddish-brown soluble powder.

*Brilliant Ponceau 4R* (Cochineal Red A) and *Fast Red D* (Amaranth) are both sodium salts of trisulphonic acids of naphthalene-azo-β-naphthol, isomeric with each other. The former is a scarlet-red easily soluble powder, the latter a reddish-brown powder.

*Roxamine* is the sodium salt of dioxyazo-naphthalene-sulphonic acid. It dyes wool red from an acid bath and is used as an orchil substitute.

B. Disazo Dyes.—(*a*) *Disazo Dyes from Azo Dye-colors* (*Primary Disazo Dyes*).—*Resorcin Brown* is the sodium salt of a sulphonic acid of resorcin-disazo-xylene-benzene. Forms a brown soluble powder.

*Fast Brown* results from the action of two molecules of α-diazo-naphthalene-sulphonic acid upon one molecule of resorcin.

*Acid Brown G* is formed by the action of hydrochloride of diazo-benzene upon chrysöidin-sulphonic acid. Dyes wool brown in acid solution.

*Bismarck Brown* is the hydrochloride of benzene-disazo-phenylene-diamine. It is much used in coloring leather.

(*b*) *Disazo Dyes from Amido-azo Dyes* (*Secondary Disazo Dyes*).—*Cloth Red G* (Azococcin 7B) results from the action of diazoazo-benzene upon α-naphthol-sulphonic acid. Forms a brown powder not readily soluble in water. Used in wool-dyeing, either alone or in connection with logwood, fustic, etc.

*Brilliant Crocëin* (Cotton Scarlet) results from the action of hydrochloride of diazoazo-benzene upon β-naphthol-disulphonic acid. Forms a reddish soluble powder.

*Biebrich Scarlet* (Ponceau B).—It is the sodium salt of amido-azo-benzene-disulphonic-acid-azo-β-naphthol. Forms a brown-red fairly soluble powder. Dyes wool and silk in acid bath a red color like cochineal.

*Crocëin Scarlet 3B* (Ponceau 4RB) results from the action of diazoazo-

benzene-monosulphonic acid upon β-naphthol-monosulphonic acid. Forms a red-brown powder dissolving with scarlet-red color. Used in wool- and silk-dyeing.

*Bordeaux G* is obtained by the action of amido-azo-toluene-monosulphonic acid upon β-naphthol-monosulphonic acid S. Dyes wool red from an acid bath.

*Naphthol Black* is the sodium salt of the tetrasulphonic acid of naphthalene-disazo-naphthalene-β-naphthol. Forms a violet-black powder. Used exclusively in wool-dyeing.

*Wool Black* is the sodium salt of the disulphonic acid of a benzene-disazo-benzene-*p*-tolyl-β-naphthylamine. It forms a bluish-black soluble powder. Dyes a deep blue-black color and is quite stable.

*Naphthylamine Black* and *Anthracite Black* are obtained by the action of disulpho-naphthylene-azo-α-naphthylamine upon α-naphthylamine and di-phenyl-*m*-phenylene-diamine respectively.

*Fast Violet* is the sodium salt of the disulphonic acid of a naphthalene-disazo-benzene-β-naphthol. Forms a dark brown soluble powder. Used in wool-dyeing.

*Chromotropes* 2*R*, 2*B*, 6*D*, etc., are combinations of diazo compounds with dioxy-naphthalene-disulphonic acid. They give colors varying from scarlet to magenta, which on subsequent treatment with a boiling solution of potassium bichromate change to very fast blacks.

(*c*) *Disazo Dyes from Diamido Compounds* (Congo Group, or Benzidine Dyes).—These dyes are distinguished from all other coal-tar dyes by the readiness with which vegetable fibres may be dyed with them without previous mordanting, so that they are equally applicable to vegetable or animal fibres, and can be used with goods of mixed fibre. They are often called *substantive cotton dyes*. Their affinity for the fibres indeed goes so far that they can be used like mordants to facilitate the fastening of other coal-tar dyes upon the vegetable fibres.

The commercial products consist generally of the potassium, sodium, or ammonium sulphonates of the dye-color.

*Naphthalene Red* is the sodium salt of naphthalene-disazo-binaphthionic acid. Dyes unmordanted cotton red from a boiling alkaline bath.

*Diamine Gold* is the sodium salt of disulpho-naphthalene-disazo-biphenetol. It dyes unmordanted cotton yellow.

*Chrysophenine* is the sodium salt of disulpho-stilbene-disazo-biphenetol. Dyes like the previous color.

By the diazotizing of this same diamido-stilbene-disulphonic acid are also derived *Hessian Yellow*, *Hessian Purple N* and *B*, and *Hessian Violet*.

The diazo compound from the molecule of benzidine is similarly combined with a series of compounds to produce the well-known benzidine dyes, *Congo G* and *P*, *Congo Yellow*, *Sulphanil Yellow*, *Brilliant Congo G*, *Cloth Brown*, *Diamine Black*, *Diamine Blue*, *Diamine Scarlet*, *Diamine Brown*, *Diamine Green*, and *Congo Corinth G*.

*Congo Red* is the sodium salt of diphenyl-*p*-disazo-naphthionic acid. Forms a reddish-brown powder, soluble in water with fine red color. This solution is so sensitive to acids that a single drop of very dilute sulphuric acid suffices to convert the whole of the liquid to a beautiful blue. It is therefore a valuable indicator in volumetric analysis.

*Benzopurpurin* is formed by the action of tetrazo-ditolyl chloride upon naphthylamine sulphonate of soda. It is a dark red powder, dissolving

easily in water. The scarlet obtained from this dye is not changed by dilute acid as is that from Congo red.

*Azo Blue* is formed by the action of tetrazo-ditolyl chloride upon β-naphthol-sulphonate of potash. It is a dark blue powder, dissolving easily in water. It is fast to acids but not to light.

Diazotized tolidine yields, besides the two dyes last mentioned, *Delta-purpurin 5B*, *Chrysamine*, *Azo Blue*, and *Azo Mauve*. Dianisidine and diphenetidine also yield, when diazotized, well-known dyes of this class, such as *Benzoaurine*, *Heliotrope*, and *Benzo-indigo-blue*.

*Carbazol Yellow* and *Naphthol Blue-black* are also colors of this class.

*Supplementary to the Azo Dyes.*—*Tartrazin* is formed by the action of two molecules of phenyl-hydrazin-*p*-sulphonic acid upon one molecule of dioxytartaric acid. Orange-yellow powder, easily soluble in water. It is a valuable woollen dye, very fast to light and fulling.

*Primuline and Ingrain Colors.*—Primuline is mentioned here because of its ready convertibility into azo colors (ingrain colors). It is the sodium salt of the sulpho- acid of a sulphated amido- compound, and is formed by the action of sulphur upon *p*-toluidine. The primuline base is a yellow powder, very soluble in hot water, and dyes unmordanted cotton direct from a neutral or alkaline bath. Its great importance, however, lies in the fact that as the sulpho- acid of a primary amine it can be diazotized (see p. 403), and then is capable of combining with the whole range of phenols and amines to form azo colors. These operations can readily be carried out upon the fibre, whence the colors so obtained have been called ingrain colors. This diazotizing and developing with the phenol or amine may be effected upon silk, wool, or cotton fibre previously dyed with the primuline base. In this way yellows, oranges, purples, reds, scarlets, maroons, and browns are produced.

When paranitraniline is diazotized we obtain azo-*p*-nitraniline. If sulphuric acid is added to the compound so formed and the diazo compound admixed with a large excess of salt, the sodium sulphate so produced protects the diazo compound from light, even in the dry state, until ready for use in the dye-bath for dyeing goods padded with naphthols, naphthylamines, etc.

5. Quinoline and Acridine Dyes.—*Quinoline Yellow* is the sodium salt of quinoline-phthalon-sulphonic acid. It forms a yellow powder, soluble in water or alcohol with yellow color. Used for wool- and silk-dyeing.

*Flavaniline* is obtained by heating acetanilid with anhydrous zinc chloride for several hours to 250° C. The commercial salt is the hydrochloride of the base so obtained. Was formerly used for wool- and silk-dyeing, and for cotton after mordanting with tannin and tartar emetic.

*Cyanine* (Quinoline Blue) is prepared by treating a mixture of quinoline and lepidine with amyl iodide. It forms a fine blue color, but unstable to light. It is not of importance in textile coloring, but is used in the manufacture of orthochromatic photographic dry plates.

*Quinoline Red* is obtained by the action of benzo-trichloride upon a mixture of quinaldine and isoquinoline. Is also employed in the manufacture of orthochromatic photographic plates.

*Acridine Yellow* is the hydrochloride of diamido-dimethyl-acridine. Dyes silk greenish-yellow with green fluorescence, and cotton mordanted with tannin yellow.

*Phosphine* (Chrysaniline) is, as was before noted (see p. 397), a by-product in the manufacture of magenta, but is probably diamido-phenyl-acridine. The phosphine of commerce is the nitrate or chlorhydrate of the base chrysaniline. Used at present chiefly in silk dyeing.

6. ARTIFICIAL INDIGO.—Artificial indigo has now become an article of commerce, and in purity and uniformity distinctly excels the natural product. The first important synthesis was that utilizing what is known as "propiolic paste," which is a moist paste containing a definite percentage (usually twenty-five per cent.) of *o*-nitrophenyl-propiolic acid prepared from synthetic cinnamic acid. Professor Baeyer found that this *o*-nitrophenyl-propiolic acid when in alkaline solution is readily changed by reducing agents, like grape-sugar, milk-sugar, sulphides, sulphydrates, and especially by xanthogenate, into indigo-blue. The reducing agents act already in the cold in either aqueous or alcoholic solutions. This "propiolic paste" was used for a time in calico-printing, being printed on the goods along with the reducing agent, but the decomposition of the xanthogenate of soda develops mercaptan, the unpleasant odor of which adheres very persistently to the goods, and the blue color is slightly gray in shade. It has therefore been given up for the present.

Kalle's artificial indigo (due to Baeyer in conjunction with Drewsen) is prepared by converting *o*-nitrobenzaldehyde into *o*-nitrophenyllacto-ketone by the action of acetone. The product of the reaction is then changed to a soluble compound by treatment with sodium bisulphite, and is sold under the name of "indigo salt." This salt, if dissolved in water or thickened with any suitable substance and afterwards applied to woollen fabrics and these passed through a solution of caustic soda of 20° B., causes the full color of indigo to develop.

Following these syntheses comes that of Heumann from phenyl-glycocoll, which, when fused with caustic alkali, yields pseudo-indoxyl, and this is easily changed into indigo by atmospheric oxidation.

Similarly, phenyl-glycocoll-*o*-carboxylic acid (from chloracetic and anthranilic acids), heated with caustic alkalies, yields the same results.

This last synthesis of Heumann and that of Baeyer and Drewsen, mentioned above, are the two which are now commercially carried out.

7. OXYKETONE COLORS $\left(\text{Chromophor } \begin{matrix} \text{O} \\ \| \\ \text{—C—} \end{matrix}\right)$.

(*a*) ANTHRAQUINONE DERIVATIVES.—*Alizarin.*—This term may be applied commercially to the pure dioxyanthraquinone found in the madder-root and made artificially from anthraquinone-monosulphonic acid, or to the two trioxyanthraquinones obtained from anthraquinone-disulphonic acid, and known more accurately as anthrapurpurin and flavopurpurin. The first or true alizarin is the blue shade alizarin. This is a yellow powder coming into commerce as a ten per cent. or twenty per cent. paste. When dried and sublimed it forms splendid orange-red crystals, melting at 280° C. It is insoluble in water and sparingly soluble only in cold alcohol. Sulphuric acid dissolves it, and on diluting the alizarin is precipitated again unchanged. It acts as a weak acid, and forms alizarates with the alkalies and metallic hydrates.

*Anthrapurpurin* (Isopurpurin), as before stated, is a trioxyanthraquinone, but is generally produced along with the preceding compound in the manufacture of commercial alizarin, as both the monosulphonic and the

disulphonic acids are obtained in sulphonating anthraquinone. Anthrapurpurin is obtained in the purest state by melting pure β-anthraquinone-disulphonic acid with caustic soda and chlorate of potash. It melts at 360° C.

*Flavopurpurin* is obtained also in the manufacture of commercial alizarin, and can be prepared as sole product by melting α-anthraquinone-disulphonic acid with caustic soda and chlorate of potash. Forms orange-colored needles, melting at over 300° C. A mixture of anthrapurpurin and flavopurpurin with little alizarin constitutes the commercial yellow shade alizarin.

*Purpurin* is also a trioxyanthraquinone, but differs in its molecular formula from both anthrapurpurin and flavopurpurin, and is therefore one of three isomers. It is not a constituent of commercial artificial alizarin, but is found accompanying true alizarin in the madder-root. It forms red needles, beginning to sublime at 150° C. and melting at 253° C. It is soluble in boiling water with dark-red color.

*Alizarin Bordeaux B* is a tetraoxyanthraquinone, and is made by oxidizing alizarin with fuming sulphuric acid and saponification of the ether so formed.

*Alizarin Cyanine R* is penta-oxyanthraquinone obtained by oxidizing the *alizarin bordeaux* in sulphuric acid with manganese dioxide and heating the intermediate sulphuric ether with dilute acid. Dyes wool mordanted with alumina violet, with chromium blue.

*Alizarin Orange* (Nitroalizarin) is formed from alizarin by the action of nitrous acid, or by the action of nitric acid of 42° B. upon alizarin suspended in glacial acetic acid. It forms a yellow paste of twenty per cent. dry material. Aluminum salts form an orange color, chromium salts a brown-red shade. Used with silk, wool, and cotton.

*Alizarin Red* is the sodium salt of alizarin-monosulphonic acid, and *Alizarin Maroon* is amidoalizarin.

*Alizarin Blue* is a dioxyanthraquinone-quinoline, and is made by heating β-nitroalizarin with glycerine and sulphuric acid to 90° C. Dark blue powder, almost insoluble in water. Hence is used either by reduction with zinc-dust, grape-sugar, or similar reducing agent and subsequent atmospheric oxidation, as in indigo-dyeing, or by forming a soluble compound with alkaline bisulphites, designated as *Alizarin Blue S.* This latter is much faster to light than the original color.

*Alizarin Indigo-blue S* and *Alizarin Green S* are similar sodium bisulphite compounds,—the first of penta-oxyanthraquinone-quinoline and the second of tri- and tetra-oxyanthraquinone-quinoline and their sulphonic acids.

*Anthracene Brown* (Anthragallol) is a trioxyanthraquinone. It is formed by heating benzoic and gallic acids with concentrated sulphuric acid, or by heating pyrogallol with phthalic anhydride and zinc chloride. It comes into commerce as a dark brown paste, and yields very fast shades.

*Ruffigallol* is a hexaoxyanthraquinone, and is made by the action of sulphuric acid upon gallic acid.

(*b*) *Oxyketone Colors other than Anthraquinone Derivatives.*—*Alizarin Yellow A* is made by the condensation of benzoic acid with pyrogallol, and is a trioxybenzophenone, while *Alizarin Yellow C* is made by the condensation of acetic acid with pyrogallol in the presence of zinc chloride. It is a gallacetophenone.

*Anthracene Yellow* is obtained by the treatment of dioxy-β-methylcoumarin with bromine.

*Alizarin Black S* is the sodium bisulphite compound of naphthazarine (dioxynaphthoquinone).

*Galloflavin* is formed by the atmospheric oxidation of gallic acid in alkaline solution. Forms a dirty-yellow paste, insoluble in water or hydrochloric acid. Wool mordanted with chromium salts takes a color resembling that obtained from fustic.

8. Dyes of Unknown Constitution.

*Cachou de Laval* is obtained by the fusion of organic substances such as sawdust, bran, etc., with sodium sulphide. It dyes cotton brown.

## IV. Analytical Tests and Methods.

In this section it is not the intention to exhaust the subject of the chemical examination of coal-tar colors, but to briefly indicate the more important and characteristic tests. The complete chemical analysis of the artificial organic dyes is very seldom resorted to, the analyst usually determining the *identity* of the coloring matter by means of the tabular schemes which have been published from time to time as new products have appeared on the market, and estimating the *moisture* of the sample and such foreign substances as the sulphates of soda, and of magnesia, salt, sugar, starch, and dextrine, sand, etc. Of considerable value in connection with the above is a dyed sample of cloth or yarn, which, although not strictly a chemical test, is one of equal importance, especially for the information of the immediate user of the dye. The recognition of dyes, either by themselves or on the fibre, is often desirable, but this requires considerable care and judgment, from the fact that a very large number are simply mixtures, some with as many as five separate dyes; in such cases the task is almost hopeless. These mixtures are sometimes made at the color manufactory, and again by the local agent; in the latter case, usually to supply some particular shade called for, and generally without any regard to the chemical nature of the constituents; this indiscriminate mixing accounts in a measure for the streakiness and uneven effects noticed in dyeing piece goods and yarn with such colors, which cannot always be detected by dyeing the small test samples in the laboratory.

*Fastness to Light* is determined by exposing one-half of a dyed skein or piece of dyed cloth to the action of direct sunlight for a definite time, say thirty days or longer.

*Fastness to Soap.*—A piece of dyed cloth or yarn is worked in a *neutral* soap lather, washed, dried, and compared with the original.

*Comparative Dye-trials.*—For this purpose vessels of glass, porcelain, or tinned copper are most convenient,—the latter is the best suited,—and if means can be had to provide heating by steam, it leaves nothing to be desired. When several comparative dyeings are to be made at one time of the same class of samples, one equal temperature is necessary.

*For Wool and Silk.*—In either case it is best to use a vessel containing about one litre. From twenty to twenty-five grammes of wool (yarn or fabric) and about five to ten grammes of silk answer well for the tests. The quantity of dye used varies, although two standards, representing one per cent. and five per cent. of the weight of the wool or silk, answer, as they give two shades which are convenient for estimating the dyeing value of

the sample. To make the test, the color is weighed out carefully, washed into the dye-bath containing water, and brought to the boil, into which the material, previously wetted out, is immersed and kept moving about for a definite time, say twenty to thirty minutes, or until the bath is exhausted of color, when it is withdrawn, washed, dried, and the shade compared with a swatch of the same weight, treated under exactly the same conditions as to temperature, time, etc.

To determine the relative dyeing values of color samples, two solutions of equal value are made of equal (known) weights of the dyes, and two dyeings are made as above, only adding the dye solution to the bath as fast as it is taken up by the fabric; a point will be reached when no more color will be taken up, when the addition must stop, the difference in the volume of the solution remaining, from their original volume, gives the amount used in each test; and as the strength was known, the relative amounts absorbed by the fabric can be calculated. The above applies equally to silk. No general rule can be given which will embrace the application of the colors to fibres in testing, reference must be had to the various classes of dyes and methods in Chapter XIV.

*For Cotton.*—Few colors are directly applicable to this fibre without previously mordanting it with suitable substances which will cause the color to remain. In the laboratory, a quantity of cotton is taken (yarn or piece), boiled well in water, and immersed in a five per cent. solution of tannin for about twelve hours, when it is removed and boiled in a bath containing two and a half per cent. of tartar emetic for thirty to forty-five minutes, washed, dried, and kept for use. (Other mordants—*e.g.*, tin, iron, alumina, etc.—are used according to the kind of work done in the establishment.) In the matter of printed goods, swatches of cotton cloth, mordanted on one piece with several bases, are made by the printer, and these are then passed through one solution of color, and the effect can be conveniently noticed.

*For Woollen Yarn Printing.*—Pastes are made up of the color in varying strengths with starch or flour, and with such assistants as may be required, such as oxalic or tartaric acids, stannous chloride, etc., in the following manner: Five grammes of color are taken and mixed with a little water containing dextrine or glycerine, and this is made up to five hundred cubic centimetres with a paste of flour (one pound per gallon). Twenty or thirty strands of yarn about a metre long are taken, held at one end, and the color-paste rubbed well in for a space of about six inches with a glass rod or spatula; one-tenth of the color-paste is emptied out, and the remaining is diluted again to five hundred cubic centimetres, and this is then applied to the yarn, leaving a space of an inch or so from the first. The diluting operation is continued so that the printings on the yarn will represent color in the proportion of 1, .9, .8, .7, etc., giving a range of shades of one color. The yarn so printed is then steamed for about twenty to thirty minutes under pressure, or longer without pressure, washed, and dried. This method is of much value in matching and valuing shades in tapestry carpets.

*By Colorimetry.*—This method involves the use of two graduated glass tubes, closed at one end, each of the same diameter, thickness, and length. The standard sample of dye being weighed and dissolved in water, is poured into one tube, while an equal weight of the sample to be tested is poured into the other, and by holding the tubes to the light the depth of color is

seen. If one is darker in shade than the other, it is diluted until the shades are equal, when, by knowing the number of cubic centimetres of water added to equalize the tint, the relative strength of the dyes can be ascertained.

*Mixtures of Dyes* can be detected by sprinkling some of the powder on the surface of distilled water, and noticing the color of the streaks formed as the particles subside, or by dissolving the dye in a little alcohol and water contained in a small evaporating dish or beaker, and immersing therein the end of a strip of white blotting-paper, when, in the case of mixtures, several differently-colored bands are seen on the paper, owing to the fact that the constituents of the mixture do not always possess the same degree of capillarity. These bands can be cut off and separately tested by proper reagents according to the scheme for identification of dyes following. Fractional dyeing has also furnished information of value; usually wool or silk being employed.

*Identification of Coal-tar Dyes.*—Weingärtner's comprehensive tables, which follow, affords means of determining the group to which a sample of dye under examination belongs. The dyes are divided conveniently into two divisions, *basic* and *acid coloring matters*, and the latter into *soluble* and *insoluble in water.*

I. *The Dye is Soluble in Water.*—Add a few drops of a solution of tannin* to a solution of the dye, and note the formation of a precipitate, after heating.

*A. Precipitation takes Place.—The color is basic.*—A small quantity of the original color is dissolved in water, and reduced with hydrochloric acid and zinc-dust, rapidly filtered, and neutralized with sodium acetate; small strips of filter-paper are immersed in the solution, and exposed to oxidize.

| THE ORIGINAL COLOR REAPPEARS ON THE PAPER. | | | | | The original color does not reappear. |
|---|---|---|---|---|---|
| Reds. | Oranges and yellows. | Greens. | Blues. | Violets. | |
| FUCHSINE, MAGENTA, ROSEINE. With *sulphuric acid*, brown.<br>NEUTRAL RED. With *sulphuric* acid, *green*. With *caustic soda solution*, yellow-brown precipitate.<br>SAFRANINE. With *sulphuric acid*, green. *Caustic soda*, brownish-red precipitate<br>PYRONINE.<br>ACRIDINE RED.<br>TOLUYLENE RED | PHOSPHINE, CHRYSANILINE. With *sulphuric acid*, reddish-yellow precipitate. Green fluorescence. *Caustic soda*, light-yellow precipitate. Solubie in ether with green fluorescence.<br>FLAVANILINE. With *sulphuric acid*, dirty yellow precipitate. Soluble in ether with blue fluorescence.<br>ACRIDINE YELLOW.<br>ACRIDINE ORANGE. | MALACHITE GREEN. VICTORIA GREEN. With *sulphuric acid*, yellow, on diluting with water, green. *Ammonia* causes gray or red precipitate.<br>BRILLIANT GREEN. With *sulphuric acid*, same as above, color reappears slowly. *Ammonia*, little or no precipitate.<br>METHYL GREEN, PARIS GREEN. With *sulphuric acid*, same as above, color not reappearing on dilution. *Ammonia*, solution decomposed, no precipitate.<br>AZINE GREEN. | METHYLENE BLUE. With *sulphuric acid*, green. *Caustic soda* causes violet-black precipitate.<br>NEW BLUE. With *caustic soda*, blue-black precipitate.<br>MUSCARINE. *Caustic soda* causes brownish-red precipitate. With *tannin*, indigo-blue precipitate.<br>CAPRI BLUE.<br>MELDOLA'S BLUE.<br>METAPHENYLENE BLUE.<br>INDAMINES. | METHYL VIOLET. *Sulphuric acid* causes a yellowish-brown coloration; on dilution changes to green and violet-blue.<br>NEUTRAL VIOLET. *Sulphuric acid* causes bright violet color; on dilution changes to blue.<br>MAUVEINE. *Sulphuric acid* causes gray color; on dilution changes to light blue and violet-red.<br>AMETHYST. *Sulphuric acid* gives green color; blue on dilution.<br>PRUNE.<br>PARAPHENYLENE VIOLET. | CHRYSOIDINE. Color, orange. In *sulphuric acid*, dissolves to a brownish-yellow solution.<br>VESUVINE. Color, brown. upon silk, orange. In *sulphuric acid*, soluble to a pale liquid.<br>AURAMINE. Color, yellow. With *alkalies*, white precipitate. On warming with *sulphuric acid*, solution decolorized<br>VICTORIA BLUE. Color, blue. In *sulphuric acid*, brownish-red, changes to bluish-green. |

* Twenty-five parts of tannin, twenty-five parts of acetate of soda, and two hundred and fifty parts of water.

### B. *No Precipitation takes Place.—The color is acid.*

<table>
<tr><td colspan="5">REDUCE WITH HYDROCHLORIC ACID AND ZINC-DUST.</td><td rowspan="5">The solution becomes brownish-red. The color of the ammoniacal solution reappears on the paper.</td></tr>
<tr><td colspan="2">The color reappears on the filter-paper.</td><td colspan="3">The color does not reappear on the filter-paper.</td></tr>
<tr><td colspan="2">The aqueous solution is acidulated with hydrochloric acid, and agitated with ether.</td><td colspan="3">The original coloring matter, when heated on platinum foil,</td></tr>
<tr><td rowspan="2">The ether takes up the color.</td><td rowspan="2">The ether remains uncolored.</td><td rowspan="2">Deflagrates without colored vapors.</td><td colspan="2">Burns without deflagrating, but with colored vapors. A piece of unmordanted cotton cloth is heated in a solution of the original dye.</td></tr>
<tr><td>The dyed cloth is treated with a warm solution of soap. The color remains.</td><td>The color is removed by the soap solution.</td></tr>
<tr>
<td>PHTHALËINS.<br><br>EOSIN. With sulphuric acid, solution yellow. By heating, hydrobromic-acid vapors are evolved. Hydrochloric acid precipitates orange-colored flakes.<br><br>SAFROSINE. Sulphuric acid causes gold-yellow solution. Hydrobromic acid evolved on heating. With hydrochloric acid, brown flakes precipitated.<br><br>PHLOXIN. Same as above. Flesh-colored precipitate with hydrochloric acid.<br><br>ROSE BENGALE. No fluorescence in water. With sulphuric acid, orange color. On heating, iodine vapors are evolved.<br><br>CHRYSOLINE. Brown-yellow solution; on adding hydrochloric acid, decolorized with formation of brown precipitate.<br><br>CORALLIN, AURIN. Brick-red solution. With hydrochloric acid, yellow precipitate. No vapors on heating</td>
<td>SULPHONATED ROSANILINE DERIVATIVES.<br><br>ACID FUCHSINE, ACID MAGENTA. Aqueous solution, bluish-red. In sulphuric acid, yellow, changing to red on dilution.<br><br>ACID GREEN. Pale green in aqueous solution. Alkalies decolorize.<br><br>ALKALI BLUES. Alkalies decolorize; restored by acids.<br><br>CHINA BLUE. Aqueous solution, blue. Alkalies have no action.<br><br>ACID VIOLET. Aqueous solution, violet. Ammonia decolorizes. In sulphuric acid, orange solution. On dilution, gray-violet.<br><br>INDULINES, NIGROSINES. Aqueous solution, grayish-violet. Blue precipitate with hydrochloric acid. With ammonia, violet-red precipitate.</td>
<td>NITRO-COLORING MATTERS.<br><br>PICRIC ACID. Aqueous solution, greenish-yellow. No precipitate with hydrochloric acid. Detonates when mixed with carbonate of soda and heated.<br><br>MARTIUS YELLOW. With hydrochloric acid, yellowish-white precipitate. Soluble in ether.<br><br>NAPHTHOL YELLOW. No precipitate with hydrochloric acid. Insoluble in ether.<br><br>AURANTIA. Concentrated aqueous solution, red; when diluted, yellow. Alkalies throw down deep-red precipitate.</td>
<td>BENZIDINE DERIVATIVES.<br><br>CONGO RED. Aqueous solution, red. In hydrochloric acid, blue.<br><br>BENZOPURPURIN. Aqueous solution, orange. In concentrated hydrochloric and sulphuric acids, brown precipitates.<br><br>AZOBLUE. Aqueous solution, violet-blue. Alkalies change to blood-red.<br><br>ERYTHROSIN. Aqueous solution, blood-red. Iodine vapors given off on heating dry.</td>
<td>AZO-DERIVATIVES.<br><br>The following color reactions are all with sulphuric acid:<br>FAST YELLOW,—Yellow.<br>TROPÆOLIN OO,—Violet.<br>AZOFLAVIN,—Red.<br>METHYL and ETHYL } BRONZE,—Yellow.<br>YELLOW N,—Blue-green.<br>LUTEOLIN,—Greenish-yellow.<br>TROPÆOLIN O,—Orange-brown.<br>MANDARIN,—Carmine-red.<br>BIEBRICH SCARLET,—Green.<br>CROCËIN SCARLET,—Indigo-blue.<br>XYLIDINE SCARLET,—Violet.<br>CROCËIN SCARLET 7B,—Blue.<br>PONCEAU SCARLET R, 4R and G,—Eosine-red.<br>COCCIN,—Fuchsine-red.<br>ROCCELLIN,—Violet.<br>BORDEAUX, R and G,—Blue.</td>
<td>ANTHRACENE DERIVATIVES.<br><br>ALIZARIN S. Aqueous solution, brownish-yellow. Ammoniacal solution, fuchsine-red.<br><br>CŒRULËIN S. Aqueous solution, olive brown. Ammoniacal solution, green.<br><br>ALIZARIN BLUE S. Aqueous solution, reddish-brown. Ammoniacal solution, greenish-blue.</td>
</tr>
</table>

**II.** ***The Dye is Insoluble in Water.*****—Treat with a five per cent. solution of caustic soda.**

| The Dye Dissolves. | | The Dye does not Dissolve. | | | | Insoluble in seventy per cent. alcohol. |
|---|---|---|---|---|---|---|
| If necessary, the soda solution is filtered, and the color discharged with zinc-dust, small slips of filter-paper are immersed in the solution, and exposed to the air. | | Soluble in seventy per cent. alcohol. | | | | Indigo. Ground fine, and reduced with *zinc-dust* and *ammonia*, yellowish solution, producing blue stains on filter-paper.<br>Aniline Black.<br>Primuline Base. |
| | | The solution is not fluorescent. | | The solution is fluorescent. | | |
| The original color of the solution reappears. | The original color does not reappear. | With thirty-three per cent. soda solution, change to reddish-brown. | With thirty-three per cent. soda solution, no change. | With thirty-three per cent. soda solution, fluorescence disappears. | With thirty-three per cent. soda solution, fluorescence remains. | |
| Gallocyanin. *Soda solution*, violet; *sulphuric acid*, blue.<br>Gallëin. In *sulphuric acid*, blue.<br>Cœrulëin. *Soda solution*, green; *sulphuric acid*, green.<br>Galloflavin. *Soda solution*, yellow; *sulphuric acid*, yellow.<br>Alizarin Blue.<br>Alizarin Black.<br>Ruffigallol. | Canarin. *Soda solution*, yellow. Insoluble in *sulphuric acid*.<br>Alizarin. *Soda solution*, blue-violet; changed to red on heating with zinc-dust.<br>Anthrapurpurin. Fuchsine red in *alkalies*.<br>Flavapurpurin. Same.<br>Chrysamin. In *soda solution*, orange. In sulphuric acid, fuchsine-red.<br>Nitroalizarin. *Soda solution*, red. Reduced with *zinc-dust*, stains paper indigo-blue.<br>Alizarin Blue. Difficultly soluble in *soda* to green solution; stains filter-paper violet.<br>Alizarin Brown. *Soda solution*, olive-brown. In *sulphuric acid*, red-brown. | Indulines and Nigrosines. In *alcohol*, solution greenish-blue. Agitated with *benzol*, shows marked brown-red fluorescence.<br>Rosaniline, or Diphenylamine Blue. *Alcohol* solution deep blue. On adding *hydrochloric acid*, becomes green. No fluorescence with benzol. | Indophenol. *Alcoholic solution*, blue. On adding *hydrochloric acid*, becomes brownish-red.<br>Sudan II. and III. | Magdala Red. *Alcoholic solution*, blue, with a cinnabar-red fluorescence. | Primrose. *Alcoholic solution* has blue-red color, with yellow fluorescence.<br>Cyanosin. *Alcoholic solution*, bluish-red, with dark-red fluorescence. | |

*Chemical Analysis of Dyes.*—*Ultimate analysis* is not within the scope of this work. *Proximate analysis* is constantly resorted to, and embraces the determination of the *moisture, mineral matter, salts, starches*, etc.

*Determination of Moisture.*—One to three grammes of the coloring matter are weighed in a shallow porcelain or platinum dish, and exposed to a temperature of 100° to 105° C. in an air-bath, allowed to cool in a desiccator, and weighed again, the difference is moisture.

*Insoluble Matter.*—The dried residue from the above is dissolved in water, warmed to facilitate solution if necessary, and filtered through a small tared filter, washed until no color remains, dried, cooled in a desiccator, and weighed. If *dextrine* is present, it will be noticed in this test by its odor.

*Sodium Chloride* (Common Salt).—This is usually determined by nitrate of silver, but as many dyes contain chlorine in the molecule, the addition of this reagent directly to the solution is inadmissible. Salt can be estimated indirectly by calculating from the amount of chlorine found in the ash left upon igniting some of the dye by dissolving in water, filtering to remove any insoluble matter, acidulating with a few drops of nitric acid, and adding nitrate of silver to complete precipitation. Then boil for a few minutes, and filter, wash well with warm water, dry on the filter, remove the precipitate carefully, and ignite the filter separately, when cool add one or two drops of nitric acid and a drop of hydrochloric acid, ignite again, and add the main bulk of the precipitate, and ignite until the edges begin to fuse, cool in a desiccator, and weigh the chloride of silver, from which can be calculated the percentage of salt. Allen states that chlorine so found probably existed originally in the dye as common salt. Another method, which does not answer in every case, is to acidulate an aqueous solution of a known weight of the dye with sulphuric acid, agitate with several changes of ether until all the color has been taken up from the aqueous solution in which the salt remains, separated by a tap-funnel, when it can be precipitated and estimated as usual.

*Sulphate of Sodium* (Glauber's Salt) in the anhydrous condition is an admirable adulterant for light-colored dyes. By adding a hot solution of barium chloride to an acidulated (hydrochloric acid) solution of a dye which is sulphonated, and contains an admixed sulphate, a precipitate of barium sulphate and barium sulphonate will be formed, this is filtered and well washed with water, and treated with a solution of ammonium carbonate, the sulphonate will be converted into barium carbonate by decomposition; upon adding dilute hydrochloric acid, the carbonate dissolves while the sulphate will remain unchanged, wash with warm water, dry, detach from the filter, ignite, and weigh.

*Sulphate of Magnesia* (Epsom Salt).—This body is to a considerable extent employed as an adulterant, and as magnesium is never a chemical constituent of tar-dyes, its presence in the ash is conclusive. The estimation is carried out by igniting the dye, dissolving in dilute hydrochloric acid, filtering if necessary, adding ammonium chloride and a slight excess of ammonium hydrate, and finally a solution of sodium ammonium phosphate, stirring, care being taken to prevent the glass rod used from rubbing the sides of the beaker, and allowing to stand overnight, filter, wash, dry, ignite, and weigh as magnesium pyrophosphate.

*Carbonates.*—Indication of presence by effervescing upon addition of a dilute acid. Estimated by use of one of the forms of carbonic acid apparatus.

*Dextrine.*—This substance is estimated by weighing one or two grammes of the dye in a small tared beaker, provided with a glass rod. The dye is dissolved in a little water, and absolute alcohol added, when the dextrine will be thrown down, and adheres closely to the glass. The contents are emptied, and the glass rinsed two or three times with alcohol, dried, and weighed.

*Starch.*—The presence of this substance must not be taken as an adulterant in every case it is found; owing to its peculiar properties it acts as a drier or absorber of moistness, and hence prevents the caking of the dye. By dissolving a quantity of the dye in water, and allowing the solution to stand in a conical glass for a while, any starch present will subside, the clear liquid is poured off, and the residue repeatedly washed with distilled water and alcohol until no color remains, it can then be examined with the microscope; a drop is placed on a slide with a drop of water, the cover-glass put on, and a drop or two of iodine solution placed on the edge, and allowed to displace the water by the aid of a piece of filter-paper opposite the iodine, will, if starch is present, develop the characteristic reaction,—blue.

*Sugar.*—Estimated as for dextrine; the alcohol used should be saturated with sugar. Sugar can be estimated in dyes by precipitating the coloring matter with basic acetate of lead, and proceeding as for raw sugar with the polariscope (see page 157), or by inverting and estimating with Fehling's solution (page 159).

*Sand and Iron Filings* are gross adulterations occasionally met with in dyes from unprincipled dealers. Their presence would have been noticed under the *insoluble matter* determination. Iron filings can be easily determined with a magnet.

A careful microscopic examination of ground and crystallized dyes will throw much light on their preparation; bronze-powder and sugar crystals have been thus found.

*Paste-dyes*, etc., are best estimated by evaporating a weighed quantity to absolute dryness in a small glass mortar, grind thoroughly, add water, and filter through a tared filter, wash with water, dry, and weigh. If this is not done, trouble will be met; paste-dyes not filtering well if simply diluted with water.

*The Examination of Dyed Fibres* can well be accomplished by the aid of the following table, which is adapted from those of Hummell,* of R. Lepetit,† and of Lehne and Rusterholz,‡ and embraces a majority of the more important coloring matters which have found application. The reagents employed are hydrochloric acid (HCl), concentrated, 21° Beaumé, and dilute, one part of acid 21° B. and three parts water; sulphuric acid ($H_2SO_4$), concentrated, 66° B., and dilute, one part of acid 66° B. and five parts of water; nitric acid ($HNO_3$), concentrated, specific gravity 1.40, dilute one part of the strong acid and two parts of water; caustic soda solution (NaOH), concentrated, 38° B., and dilute, one part of the strong solution and ten parts of water; ammonia, specific gravity .960; alcohol ninety-six per cent.; stannous chloride, tin salt ($SnCl_2 + 2H_2O$), and concentrated hydrochloric acid equal parts; acetate of ammonia solution, by neutralizing ammonia with pure acetic acid and bringing exactly to 5° B.

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* Hummell, The Dyeing of Textile Fabrics, London, 1885.

† R. Lepetit, Journ. Soc. Chem. Ind., vol. viii. p. 773 (from Zeits. f. angew. Chem., 1888, 535).

‡ Färber-zeitung, 1891, Hefte 11, 13, etc.

The initials or names in parentheses following the names of the dye-colors are those of the manufacturers who furnish the particular dyestuff, and will be readily understood by those accustomed to handle these wares.

A separate column has not been made for nitric acid, but where its action is distinctive it is noted under the head of remarks.

*Method of Procedure.*—For the testing with concentrated acids and caustic alkalies small watch-crystals are most advantageously used. These are then placed upon white paper in order to be able to observe carefully the changes of color. The concentrated acids are most conveniently dropped from small dropping tubes or pipettes, so that they can be added drop by drop until the fibre is completely covered. After addition of the acids four to five minutes are allowed, and the action is then noted. The watch-crystals are then heated carefully by using a very small flame or placing them upon a steam-coil, but the liquids upon the watch-crystals should not be allowed to boil. After waiting a few minutes and allowing them to cool, water is added to the contents of the watch-crystals.

All the other reactions of the tables are carried out in test-tubes. The fibre is placed in the test-tube, covered with the reagent, and allowed to stand for several minutes, then heated without quite bringing the liquids to the boiling-point, when the action is carefully noted. Finally the liquids are boiled for a short time. The solution is then poured off and caustic alkali or acid, as the case may be, is added, and any change carefully noted. After the tests with concentrated hydrochloric or sulphuric acids the fibres are well washed with water in order to observe whether the original color is thereby restored.

## DETECTION OF COLORING MATTERS ON THE FIBRES.

For this test, small portions of the dyed fabric, or fibres, are placed in the several reagents, contained in porcelain evaporating dishes, and the reaction noted.

### *Red Dyes.*

| Name of Coloring Matter. | HCl. | $H_2SO_4$. | NaOH. | $NH_4OH$. | $SnCl_2$ + HCl. | Alcohol. | Remarks. |
|---|---|---|---|---|---|---|---|
| Acid Magenta. (B. A. S. F.—R. H. and S.) | Bluish-red liquid extracted; color of fibre unchanged. | Same as with HCl. | Decolorized in the cold. | Same as with NaOH; color restored on exposure. | Color extracted on boiling. | But little extracted. | |
| Alizarin. | Dilute, no action; concentrated, fibre bright yellow, liquid amber-yellow. | Dilute, no action; concentrated, *red color* extracted. Concentrated $H_2SO_4$ at ordinary temperature entirely dissolves cotton dyed with alizarin-red, and the alizarin separates out as a flocculent precipitate, which can be collected, dried, and sublimed. | Fibre and solution violet. | No action. | Fibre orange-yellow, liquid bright yellow. | No action | Gives no fluorescent solution on boiling with $Al_2(SO_4)_3$. (Distinction from madder and purpurin.) Bleaching-powder and chromic acid bleach it. Boiled with $Ba(OH)_2$ solution, fibre becomes violet. $HNO_3$ gives yellow spot. An alkaline solution of $K_3FeCy_6$ has no action, nor has $K_2Mn_2O_8$. $HNO_3$ vapor converts it into yellow nitro-alizarin. On heating, alizarin-red loses brilliancy and becomes brownish, but regains most of the brilliancy on exposure to air. The ammoniacal, aqueous, or alcoholic solutions give characteristic absorption spectra. |
| Aurin. | Fibre yellow. | Same as with HCl. | Solution bright red. | Same as with NaOH. | In the cold, solution yellow. | Color extracted. | |
| Benzopurpurin B. (Bayer.) | Dilute HCl, fibre reddish-brown, solution colorless. Concentrated HCl, fibre dark brown. | Fibre black-blue, solution blue-black; on dilution changes to violet. | No reaction. | No reaction. | Fibre brownish-red, pink, and finally decolorized. | Extracts traces of color. | Nitrous acid, fibre brownish-black. Picric acid, fibre reddish-brown. All these dyes which resist NaOH are attached by a hot soap solution. |
| Benzopurpurin 2B. (Bayer.) | Dilute HCl, fibre blue-black, solution colorless. Concentrated HCl, same. | Fibre black-blue, solution dark blue; on dilution blue. | No reaction. | No reaction. | Fibre blue-black, light gray, finally colorless. | No reaction. | Nitrous acid, fibre blue-black and violet. Picric acid, fibre dark brown. |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| BIEBRICH SCARLET. | Fibre violet, liquid colorless; liquid becomes greenish-blue on standing. | Fibre and solution green. | Fibre dark bluish-red, liquid colorless. | No reaction. | Fibre decolorized. | Little or no action. | $HNO_3$ gives a dark-blue spot, which changes to brown with a dark-blue border. |
| BRILLIANT CONGO. (Bayer.) | Dilute HCl, fibre brown-red, solution colorless. Concentrated HCl, fibre blackish-violet with a reddish tint. | Fibre blue-black, solution blue; on dilution purple-violet. | No action. | No reaction. | Fibre brownish-red, becomes decolorized. | Extracts some color. | Nitrous acid, fibre black; turns black-violet with ammonia. Picric acid, fibre brown. |
| CARMOISINE. (Bayer.) | Dilute HCl, no reaction. Concentrated HCl, fibre dark violet; original color restored on washing. | Fibre and solution blackish-violet. | Fibre turns slightly brown, solution light pink. | Fibre unaltered, solution pink. | Little action in the cold; on heating, fibre is decolorized. | No action. | $HNO_3$, brown-violet spot, disappearing on washing. |
| CONGO CORINTH. (Bayer.) | Dilute and concentrated HCl, fibre black. | Fibre black, solution dark blue. | Fibre reddish-blue, solution colorless; color appears on washing. | Fibre reddish, solution pale pink. | Fibre black, blue, gray, and finally colorless. | Solution scarcely colored. | Nitrous acid, fibre dark blue; washed with ammonia turns magenta-red. |
| CONGO RED. (Berlin. Act. Ges.) | Fibre at once bluish-black, solution colorless. | Fibre bluish-black, solution dark-blue; turns blue-black on dilution. | Little change, solution colorless. | No reaction. | Fibre blue-black, blue, gray, and finally colorless. | No reaction. | Nitric acid, blackish-blue spot, original color restored by ammonia. Nitrous acid, fibre reddish-brown; ammonia does not restore original color, but turns the fibre brownish-purple and the solution bluish-red. Picric acid fibre bluish-black. |
| CROCEIN SCARLET 7B. (Bayer.) | Fibre at first violet, liquid colorless; on standing, fibre becomes blue, liquid greenish-blue. | Concentrated acid, fibre and solution blue. | Fibre blue. | | Fibre decolorized. | Little or no action. | Nitric acid gives at first a dark-blue spot, which changes to bright yellow with a greenish-blue border. |
| DELTA-PURPURIN 5B. (Bayer.) | Dilute, fibre reddish-brown; concentrated, fibre olive black. | Fibre dark brown, solution dirty green; reddish-brown on dilution. | No reaction. | No reaction. | Fibre first brown, gradually colorless. | Extracts some dye. | |
| DELTA-PURPURIN G. (Bayer.) | Dilute, fibre brown-red, solution colorless; concentrated, fibre greenish-black. | Fibre blue-black, solution dark blue; on dilution at first gray, then brown-red. | No reaction. | No reaction. | Fibre dark brown, then lighter, then pink, and finally colorless. | No reaction. | Nitrous acid, fibre violet-black; turns violet-red on the addition of ammonia. Picric acid, fibre brownish-red. |
| DIRECT RED. (Geigy.) | Dilute, fibre black-violet; concentrated, fibre blue, solution colorless. | Fibre blackish-blue, solution black-violet; on dilution grayish-blue. | Fibre darker, and assumes a blue tint, solution pale brown-red. | Fibre brilliant red, solution scarcely reddish. | Decolorized. | No reaction. | Nitrous acid, fibre reddish-brown; unchanged by ammonia. Picric acid, brown spot. |

*Red Dyes.*—Continued.

| NAME OF COLORING MATTER. | HCl. | $H_2SO_4$. | NaOH. | $NH_4OH$. | $SnCl_2 + HCl$. | Alcohol. | Remarks. |
|---|---|---|---|---|---|---|---|
| EOSIN A. | Fibre pale yellow. | Fibre bright yellow at once. | Fibre yellow, solution pink, fluorescent. | Fibre yellow, solution yellow, fluorescent. | Fibre orange-yellow, solution pale yellow. | *Soluble* eosins not extracted if well dyed. *Spirit* eosins readily extracted by absolute alcohol. | Hot water containing a little $NH_4OH$ extracts a pink liquid from soluble eosins. |
| HESSIAN PURPLE N. (Bayer.) | Dilute fibre black, solution colorless. | Fibre black, solution blue; after dilution grayish-blue. | No reaction. | No reaction. | Fibre black, then colorless. | Scarcely colored. | Nitrous acid, fibre violet-black; brown-red with ammonia. Picric acid, fibre brown. |
| MAGDALA RED. | No reaction. | No reaction. | No reaction. | No reaction. | Little action; fibre slightly blue. | Little extracted; solution pink fluorescent. | To detect in presence of eosin, extract in boiling alcohol,—this removes eosin, which is then tested; wash the fibre or fabric, and test for Magdala red. |
| MAGENTA. (FUCHSINE.) | Fibre and solution yellow; original color restored on washing. | Same as with HCl. | Fibre paler, afterwards colorless. | Decolorized. | Almost decolorized; color partly restored on boiling. | A bluish-red color extracted. | Sodium sulphide decolorizes. To distinguish from orchil and aurin: *Amyl alcohol* extracts a blue-red color from material dyed with magenta, but extracts a yellow color from aurin, while from orchil a pink or violet color is obtained. An *alcoholic extract* of magenta is decolorized with $NH_4OH$, while one of aurin is turned bluish-red. Orchil remains unchanged. |
| ORSELLIN 2B. (Bayer.) | Fibre first black-violet, finally black, solution pale indigo-blue. | Fibre blackish-blue, solution indigo-blue; reddish-violet on dilution. | Fibre violet, solution reddish-violet. | Same as preceding. | Slowly decolorized in the cold, rapidly on heating. | No reaction. | Nitric acid, violet spot; disappears on washing. |
| PHLOXIN J. | Fibre yellow. | Fibre yellow. | Fibre and solution pink. | Same as preceding. | Yellowish on boiling. | | |
| PRIMULINE. (POLYCHROMINE.) (CUPOLA.) | Fibre and solution red-brown. | Fibre black-violet, solution same; becomes red on dilution. | Fibre dirty dark brownish-red. | No reaction. | Fibre turns gradually reddish-brown. | No reaction. | Fast to soap, light, and acids of ordinary dyeing strength. |
| PURPURIN. | Boiled, fibre orange-yellow, solution yellow. | Same as preceding. | Heated, fibre and solution cherry-red. | Boiled, solution pale pink, fibre not changed. | Brownish-red, solution amber-yellow. | Solution red. | Nitric acid gives a bright yellow spot. Bleaching powder bleaches it. Boiled with a solution of $Al_2(SO_4)_3$ and cooling, gives an orange fluorescent solution. |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| RHODAMIN. (B. A. S. F.) | Fibre brick-red, solution colorless; color restored after washing. | Same as preceding. | Fibre little darker, with bluish tint, solution uncolored. | Fibre little darker, solution slightly pink and fluorescent. | No action in cold; on heating, solution becomes brown-red; solution slightly pink. | Extracts some dye; fluorescent solution. | Nitric acid, orange spot, disappearing on cooling. Nitrous acid, no reaction. |
| SAFRANIN. | Concentrated, fibre blue. | Fibre black, changes to green. | Solution pink. | Same as preceding. | Decolorized on heating. | Color extracted; red fluorescence. | |
| SCARLET 2R. (M. L. and B.) | Nearly decolorized on boiling; much color extracted. | Dilute, no action: concentrated, color extracted. | Nearly decolorized. | Fibre paler. | Decolorized. | Little or no action. | Nitric acid gives violet spot, which changes to bright yellow. |
| SCARLET 3R. (M. L. and B.) | Fibre not changed on boiling, solution bluish-red. | No action. | Nearly decolorized. | Little effect. | Fibre decolorized. | Little or no action. | With nitric acid, same as for Scarlet 2R. |
| *Yellow and Orange Dyes.* | | | | | | | |
| AURAMIN. | Fibre nearly decolorized, solution colorless; on dilution original color restored. | Fibre decolorized, solution colorless. | Fibre decolorized, solution colorless; after washing, color partly restored. | Fibre pale yellow, solution colorless. | Gradually decolorized in cold, quickly on heating. | No reaction. | Nitric acid, white spot; gradually turns orange in the centre. |
| BRILLIANT YELLOW. | Concentrated, fibre dark yellow. | Fibre black-violet, solution violet. | Fibre cherry-red, solution slightly pink. | Same as preceding. | Fibre dirty yellow; gradually decolorized. | No reaction. | |
| CHRYSAMIN (Bayer.) | Dilute, fibre pale yellow, concentrated, fibre reddish-brown, solution pink, yellow on dilution. | Fibre magenta-red, solution red-violet. | Fibre dark orange. | Fibre light orange, solution colorless. | Slowly decolorized. | No reaction. | Nitric acid, brown spot; gradually turns reddish-gray. |
| CHRYSOÏDINE. | Fibre red. | Yellow color extracted. | Paler and yellower. | Fibre yellower. | Almost decolorized. | Yellow color extracted. | |
| CHRYSOPHENIN. (Bayer.) | Concentrated, fibre blackish-violet, solution scarcely colored. | Fibre brown, then dark red-violet, blue on dilution. | Solution pale yellow; no change to fibre. | No reaction. | Fibre brownish-yellow, then decolorized. | No reaction. | Nitric acid, violet spot. |
| FAST YELLOW. (B. A. S. F.) | Red. | Fibre brownish-red, solution red. | Solution brownish-yellow. | Little or no action. | Fibre bright red, finally decolorized. | Some color extracted. | Nitric acid, bright red spot. |
| HESSIAN YELLOW. (Bayer.) (Leonhardt.) | Dilute, fibre lighter, concentrated, fibre blackish-blue, solution violet. | Fibre dark violet, solution red-violet. | Fibre dark red, solution light pink. | Fibre dark orange, solution slightly colored. | Pale yellow, gradually decolorized. | No reaction. | |



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*Yellow and Orange Dyes.*—Continued.

| Name of Coloring Matter. | HCl. | $H_2SO_4$. | NaOH. | $NH_4OH$. | $SnCl_2 + HCl$. | Alcohol. | Remarks. |
|---|---|---|---|---|---|---|---|
| Naphthol Yellow. | Decolorized almost completely. | Same as preceding. | Fibre orange, solution yellow. | Fibre paler, color extracted on boiling. | Fibre and solution decolorized. | Some color extracted. | Water extracts the color, $H_2SO_4$ decolorizes the yellow solution. Boiling cyanide of potassium extracts a red color. Loses color when heated on the fibre. |
| Orange No. 2. | Bluish-red. | Same as preceding, —bluer. | Fibre deep red. | No reaction. | Decolorized. | No reaction. | |
| Orange No. 3. | Fibre red, solution pink. | Bright bluish-red. | Fibre dull yellowish-red. | Solution slightly yellow, fibre unchanged. | Decolorized. | But little color extracted. | |
| Orange No. 4. | Fibre reddish-violet, solution violet. | Same as preceding. | No reaction. | Solution slightly yellow, fibre unchanged. | At first fibre becomes deep violet on heating, gradually lighter, and finally decolorized. | Yellow color extracted. | |
| Phosphine. | Fibre nearly decolorized, solution yellow. | Solution greenish-yellow. | Fibre paler and yellower. | Fibre paler and bright yellow. | Nearly decolorized. | Little color extracted. | |
| Picric Acid. | Color extracted on boiling, solution greenish-yellow. | Decolorized. | Fibre becomes orange, solution yellow. | Fibre paler, color extracted on boiling. | Decolorized. | Color extracted. | Picric acid has a bitter taste. Heated with cyanide of potassium becomes red. In compound colors, should be extracted with alcohol and tested with cyanide as above. |
| Primuline Orange. | Fibre reddish-brown, solution same. | Fibre orange-brown, solution dark red. | Fibre dark red-brown, solution scarcely colored. | No reaction. | Fibre orange-brown, then decolorized. | Some color extracted. | Nitric acid, red-brown spot. |
| Primuline Yellow. | No reaction. | Fibre dark yellow, then pale yellow. | Fibre orange-yellow, colorless solution. | No reaction. | Little action. | No reaction. | Nitrous acid, fibre dark orange, and on addition of ammonia orange-brown. β-Naphthol turns dyed fibre red. |
| Quinoline Yellow. (B. A. S. F.) | Fibre more yellow, solution colorless; on dilution, original color of fibre is restored. | Same as preceding. | Fibre at first dark yellow, and gradually decolorized; color restored on washing. | Little action. | On heating, solution becomes yellow, fibre pale yellow. | No reaction. | |
| Tartrazine. (B. A. S. F.) | Fibre orange, solution yellow. | Same as preceding. | Fibre orange, solution orange-yellow. | Same as preceding. | Decolorized on heating. | No reaction. | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| TOLUYLENE ORANGE R. (K. Oehler & Co.) | Dilute, fibre pink, concentrated, fibre paler, solution yellow; on dilution fibre turns pink. | Fibre and solution yellow. | Fibre orange, solution colorless. | No reaction. | Fibre at first pink, then decolorized on heating. | No reaction. | Nitric acid, red-violet spot turns gray. Nitrous acid, fibre grayish, on adding ammonia reddish-gray. |
| TOLUYLENE ORANGE G. (K. Oehler & Co.) | Dilute, no reaction; concentrated, fibre violet, solution reddish; on dilution fibre and solution assume original color. | Fibre magenta-red, solution slightly colored. | Fibre light orange, solution scarcely colored. | No reaction. | Fibre pink, decolorized on heating, solution colorless. | No reaction. | Nitrous acid, fibre turns gray, on adding ammonia becomes dirty yellow. |
| | | | | *Green Dyes.* | | | |
| CŒRULEIN. (B. A. S. F.) | Fibre duller, solution claret-red. | Same as preceding, solution dirty yellow. | No reaction. | No reaction. | Fibre brownish-red, solution brown; color gradually restored on washing. | No reaction. | Nitric acid, brown spot. |
| RESORCIN GREEN. | Fibre yellowish-gray, solution orange-red. | Fibre and solution light brown. | Fibre dark green, solution pale green. | No reaction. | Slight decolorization, solution brown. | No reaction. | Nitric acid, yellow-brown spots. |
| VICTORIA GREEN. (MALACHITE GREEN.) | Fibre and solution bright orange; color restored on washing with water. | Fibre nearly decolorized, solution bright orange. | Decolorized. | Decolorized. | Fibre almost decolorized, liquid yellow. | Color extracted. | |
| | | | | *Blue Dyes.* | | | |
| ALIZARIN BLUE. | Fibre violet, solution yellowish-red. | Dilute, fibre violet, solution slightly red, concentrated, violet solution. | Fibre bluish-green. | No reaction. | Fibre at first violet, brownish-red on heating, solution brown. | No reaction. | Nitric acid, yellow spot, afterwards brown. Soap and bleaching-powder, no action. |
| ALKALI BLUE. | Fibre greenish-blue, solution almost colorless. | Fibre and solution reddish-brown on standing. | Fibre reddish-brown, afterwards decolorized. | Decolorized. | Fibre not changed, colorless solution. | Color extracted by *absolute* alcohol. | Nitric acid gives a light-green spot with black border. |
| AZO BLUE. (Bayer.) | Concentrated fibre, blackish-blue, colorless solution. | Fibre bluish-black, blue solution. | Fibre cherry-red, solution pale pink. | Fibre violet-red, pink solution. | Fibre, blue-black, slowly decolorized. | No reaction. | Picric acid, fibre blackish-brown. |
| BASLE BLUE. | Fibre dark-gray, solution yellow, blue on dilution. | Fibre blue-black, green, finally yellow, solution yellow, blue on dilution. | Fibre darker. | No reaction. | No reaction. | Solution pale blue. | Nitric acid, black spot. |

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*Blue Dyes.*—Continued.

| NAME OF COLORING MATTER. | HCl. | $H_2SO_4$. | NaOH. | $NH_4OH$. | $SnCl_2 + HCl$. | Alcohol. | Remarks. |
|---|---|---|---|---|---|---|---|
| BENZOAZOMINE G. (Bayer.) | Fibre blue-black, colorless solution. | Fibre black-blue, solution greenish-blue, reddish-blue on dilution. | Fibre dark red, solution pink. | Fibre dark-violet, solution cherry-red. | Decolorized. | No reaction. | Boiled with soap, solution turns blue. |
| INDOPHENOL BLUE. | Fibre grayish-brown. | Same as preceding. | No reaction. | No reaction. | Decolorized. | Blue color extracted. | Heated with olive oil, purple color extracted. |
| INDULINE. | Fibre violet, solution deep blue. | Solution dark blue. | Red-violet color extracted, zink-dust added decolorizes solution; violet color restored by exposing the filtered solution to the air. | Same as preceding. | Extracts a violet or green color. | Bluish-violet color extracted. | Induline NN is not changed by bleaching-powder. Nitric acid gives a dark bluish-green spot. |
| METHYLENE BLUE. | Fibre nearly decolorized, solution bluish-green. | Fibre and solution green. | Fibre bluish-violet. | No action. | Decolorized. | Greenish-blue color extracted. | Nitric acid, green spot. Bleaching-powder changes it to green, and finally decolorizes it. On cotton it is faster than most anilines, resisting action of soaps, light, and weak bleaching-powder. |
| NAPHTHYLENE BLUE G. (Bayer.) | Fibre brownish-violet, solution brown-orange. | Fibre brown-black, solution dark brown, blue on dilution. | Fibre brown, solution brown-orange. | Fibre brownish-violet, solution pink | Fibre decolorized. | Solution pale violet. | HCl vapors change color of fibre to a chocolate-brown. |

*Violet Dyes.*

| NAME OF COLORING MATTER. | HCl. | $H_2SO_4$. | NaOH. | $NH_4OH$. | $SnCl_2 + HCl$. | Alcohol. | Remarks. |
|---|---|---|---|---|---|---|---|
| ALIZARIN. | Fibre and solution dull yellow. | Same as preceding. | Fibre bluer. | No reaction. | Same as with HCl. | No reaction. | Destroy color by boiling with HCl, wash, and add NaOH; the alizarin on the fibre is dissolved with purple color. |
| AZO-VIOLET. | Dilute, fibre bluer, concentrated, fibre blackish-blue, solution colorless. | Fibre black-blue, solution blue-green. | Fibre red, solution colorless. | Fibre dark violet, solution pale magenta-red. | Fibre slowly decolorized. | No reaction. | Picric acid, fibre black. Dilute acetic acid, fibre blue |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| FAST VIOLET. | Fibre blue-black. | **Fibre black, solution gray-blue, greenish-blue, finally red on dilution.** | Fibre black-blue, solution pale violet. | Fibre unchanged, solution pale violet. | Fibre decolorized. | Little action. | Nitric acid, blue-black spot. |
| GALLOCYANINE. | Unchanged. | Fibre dark blue, solution intensely blue, magenta-red on dilution. | Fibre black-violet, solution dirty purple. | Same as preceding. | Fibre gray, solution colorless. | No reaction. | Nitrous acid, fibre dirty gray-violet, solution blue green, green, finally yellow. |
| HELIOTROPE. | Dilute, fibre dark violet, concentrated, fibre black-blue, solution light blue, violet on dilution. | Fibre black-blue, solution blue. | Fibre dark red, solution colorless. | No reaction. | Fibre dark gray, slowly decolorized. | No reaction. | Nitrous acid, fibre greenish-gray, washed and treated with ammonia turns bluish-orange, solution pale brown. Picric acid, fibre dark brown. |
| METHYL VIOLET. | Fibre yellowish-brown, liquid amber-yellow; on diluting with water violet color restored. | Same as preceding. | Fibre at first pale reddish-violet, afterwards decolorized. | Fibre pale lilac, nearly decolorized. | Fibre green, nearly decolorized on standing, solution yellowish-green. | Color extracted. | |
| MUSCARINE. | Fibre blue-black, solution dirty-blue. | Fibre greenish-black, solution greenish, dirty violet on dilution. | Fibre brownish-black. | Fibre violet-blue, solution pale violet. | Fibre blackish; on heating, blue, green, finally yellowish-gray. | No reaction. | Nitric acid, black spot. |
| | | | *Brown Dyes.* | | | | |
| ALIZARIN. | Fibre brownish-orange; color restored by ammonia. | Same as preceding. | Action slight, fibre bluer, solution tinted bluer. | Unchanged. | Same as with HCl. | No action. | |
| BENZO-BROWN. (Bayer.) | Dilute, fibre reddish-brown, concentrated, fibre darker, solution purple-red. | Fibre brown-black, solution dark brown. | No reaction. | No reaction. | Fibre lighter and yellowish, solution brownish-yellow. | Little color extracted. | |
| BISMARCK-BROWN. | Fibre reddish-brown, solution red. | Same as preceding, darker. | Fibre brownish-yellow. | Fibre unchanged, solution brown. | Almost decolorized. | Red or pink color extracted. | Boiling water extracts color, glacial acetic acid more so, with yellowish-green fluorescence. |
| FAST BROWN RG. (Berlin. Act. Ges.) | Fibre dark red-violet, solution violet; on dilution fibre becomes brown again. | Same as preceding. | Fibre brilliant dark red, solution cherry-red. | Same as preceding. | Fibre darker, and quickly decolorized on boiling. | No reaction. | Nitric acid, black spot, quickly turning to light red-brown. |
| NAPHTHYLAMINE BROWN. | Fibre brownish-yellow, solution orange. | | | Fibre yellow. | Fibre purple, solution pale pink. | Solution bluish-pink. | |

*Black Dyes.*

| Name of Coloring Matter. | HCl. | $H_2SO_4$. | NaOH. | $NH_4OH$. | $SnCl_2 + HCl$. | Alcohol. | Remarks. |
|---|---|---|---|---|---|---|---|
| Alizarin Black. (B. A. S. F.) | Fibre unchanged, solution pale greenish-blue. | Same as preceding. | Fibre unchanged, solution pale blue. | No reaction. | No reaction in cold: fibre brown on boiling; solution yellow. | No reaction. | Nitric acid, after a while dark olive-green spot. |
| Aniline Black. | No action, or color becomes greenish-black; restored by alkalies; acid solution brownish. | Same as preceding. | No action. | No reaction. | Fibre greenish-gray; color restored by ammonia. | Brownish-red color extracted. | Bleaching-powder changes color to brownish-red; weak oxidizing agents have no action. |
| Naphthol Black. (M. L. and B.) | Fibre unchanged, solution reddish. | Fibre unchanged, solution olive-green. | Fibre unchanged, solution pale red. | No reaction. | Boiling, fibre light green, blue after washing. | No reaction. | Nitric acid, brown spot after a time. This dye is a mixture. |
| Resorcin Black. | Fibre drab, solution orange-brown. | Fibre and solution brown. | Fibre unchanged, solution green. | No reaction. | Fibre and solution light brown. | No reaction. | Nitric acid, brown-yellow spot. |
| Wool Black. (Berlin. Act. Ges.) | Fibre unchanged, solution light blue, pink on dilution. | Same as preceding. | No action in cold: dark violet on boiling; solution violet. | No reaction. | Fibre decolorized. | No reaction. | Nitric acid, light red-brown spot. |

# V. Bibliography and Statistics.

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## STATISTICS.

1. **Crude Materials of the Color Industry.**—Schultz (Chemie des Steinkohlentheers, 1900, 3d ed., p. 9) states that the present production of coal-tar throughout the world is as follows: England, 660,000 tons; Germany, 160,000 tons; France, 80,000 tons; Belgium, 50,000 tons; Holland, 30.000 tons; America, 120,000 tons; total, 1,100,000 tons.

As raw material for the alizarin industry, Germany imported in 1899 4,365,200 kilos. of anthracene. She also imported in the same year 3,775,-600 kilos. of naphthalene and 3,968,100 kilos. of crude carbolic acid.

The German exportations of products of this industry have been during recent years:

| | 1897. | 1898. | 1899. |
|---|---|---|---|
| Aniline oil and salts, metric centners . . . . | 91,779 | 123,603 | 122,754 |
| Aniline and similar dyes, metric centners . . | 176,389 | 197,123 | 227,046 |
| Alizarin, metric centners . . . . . . . . . | 86,408 | 93,205 | 95,869 |

In 1898 the value of the aniline colors exported was given as 72,000,000 marks. Of this amount the United States took 15,600,000 marks; England, 14,600,000 marks; Austria-Hungary, 7,000,000 marks; and Italy, 4,500,000 marks. (United States Consular Reports, November, 1899, p. 380.)

2. **Aniline and Similar Dye-colors.**—The following is the estimated daily production of aniline:

| | Pounds. | |
|---|---|---|
| England . . | 5,000 | |
| France . . . | 10,000 to 12,000 | (two-thirds exported to Germany and Switzerland). |
| Germany . . | 18,000 | |

The value of the aniline and similar dyes imported into England and the United States for recent years has been as follows:

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| England . . . . . | £485,003 | £471,543 | £519,293 | £493,569 |
| United States . . . | $3,072,915 | $3,196,478 | $3,689,214 | $3,799,353 |

3. **Alizarin.**—The importations of alizarin into the United States and into England have been for recent years as follows:

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| England . . . . . . . | £256,344 | £223,875 | £219,766 | £215,228 |
| United States . . . . . | $994,230 | $1,022,970 | $886,332 | $700,485 |

Schultz states that there are at present nine alizarin-works in full and continuous operation, of which six are in Germany and three in England, while three other alizarin-works exist which are closed at present.

# CHAPTER XIII.

## NATURAL DYE-COLORS.

### I. Raw Materials.

THE raw materials to be described here are a series of vegetable dyes coming into commerce partly as compact heart woods and roots and partly as masses of separated coloring matters, together with a few dried animal remains yielding coloring matters. We shall take them up most conveniently in groups according to the colors yielded.

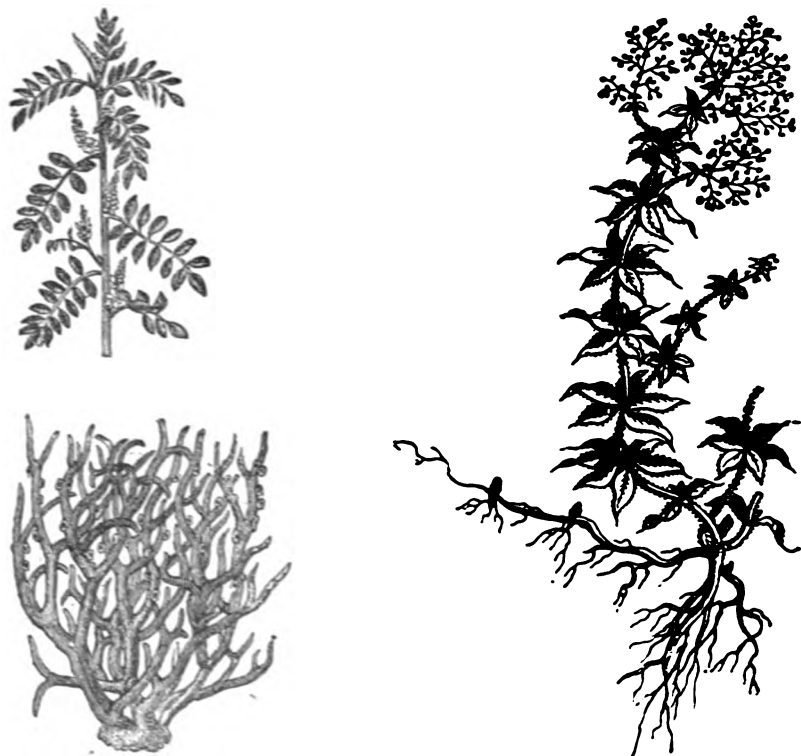
*A.* RED DYES.

1. *Brazil-wood and Allied Woods* (syn. *Rothholz, Bois de Brésil*).—The various species of *Cæsalpinia* yield woods which appear to contain a common chromogen, *brasilin*, $C_{16}H_{14}O_5$. This seems already in the wood to be changed in part into the corresponding coloring matter, *brasilëin*, $C_{16}H_{12}O_5$. And the change may be made complete by oxidizing the alkaline brasilin solution in the air or by acting upon a hot solution of brasilin with an alcoholic iodine solution. Liebermann and Burg ascribe to the crystals of brasilin the formula $C_{16}H_{14}O_5 + H_2O$, and call attention to the fact that it bears the same relation to hæmatoxylin, $C_{16}H_{14}O_6$ (see p. 448), that alizarin bears to purpurin. The best known varieties of the wood are known by the following special names: Pernambuco-wood, from *Cæsalpinia crista*, grown in Brazil and Jamaica, yellowish-red in the interior, becoming red and reddish-brown on the surface. Brazil-wood, from *Cæsalpinia Brasiliensis*, grown in Brazil, as well as the Antilles and Bahamas, is brick-red in the interior, becoming brown-red on the surface. It is inferior in coloring power to Pernambuco-wood. Sapan-wood, from *Cæsalpinia sappan*, grown in Siam, China, Japan, Ceylon, and the Indian Archipelago is somewhat lighter in color than the other varieties. It is yellowish-red in the interior and bright red on the surface. Lima-wood, or Nicaragua-wood, from *Cæsalpinia bijuga*, is grown in Central America and the north coast of South America. The Santa-Martha-wood of Mexico and Peach-wood are by some writers considered as of the same species as Nicaragua-wood, and by others are derived from *Cæsalpinia echinata*. They have a dirty-red color in the interior, becoming paler on the surface. Bahia-wood, California-wood, and Terra-Firma-wood are other less known varieties of the same class.

2. *Sandal-wood, Caliatur-wood, Bar-wood*, and *Cam-wood* (syn. *Santelholz, Bois de Santal rouge*) form another group of woods which are alike in many particulars and contain probably the same coloring matter, *santalin*, $C_{17}H_{16}O_6$. They differ as a class from the Brazil-woods in their more resinous characters, and are often known as "close woods" in contrast to the others as "open woods." The Sandal-wood (Red Sanders), from *Pterocarpus santalinus*, is grown in the East Indies, Ceylon, and Madagascar, and is a very hard and heavy wood, dark brown on the surface and blood-red in the interior. Caliatur-wood comes also from the East Indies, and though used as a substitute for the sandal-wood is considered as a distinct variety.

Sandal-wood is said to contain some sixteen per cent. of santalin. Bar-wood, from *Baphia nitida*, comes from Sierra Leone, Africa, and is a dark-red wood, containing twenty-three per cent. of santalin. Cam-wood (or Gaban-wood) is supposed by many to be the same as bar-wood, but by others is ascribed to species of *Pterocarpus*. It comes, like bar-wood, from the west coast of Africa. Madagascar-wood is a minor variety resembling Caliatur-wood.

3. *Madder* (syn. *Krapp, Racine de Garance*) is the dried and broken root of the *Rubia tinctorium* and allied species. It grows wild in Asia Minor, Greece, and the Caucasus, and has been cultivated in France, Alsace, Silesia,

FIG. 116.

Hungary, Holland, etc. The appearance of the plant may be seen from Fig. 116, in which it forms the right-hand illustration.

In the Levant, the five- to six-year-old plants are plucked, in Europe, those two to three years old. While the Turkish madder (known as Lizari or Alizari) was the earliest in use, the French variety grown in the neighborhood of Avignon, in part upon marshy soil (*palus*) and in part upon soil containing lime (*rosée*), has long been considered the best. Other varieties are the Dutch or Zealand madder, the Alsatian, the Silesian, and the Russian madder. That which has not been freed from the brown outer crust before grinding is inferior to that which has been so freed, and which is known as "crop-madder," while the impurest variety, obtained by grinding the rootlets, crusts, and woody parts of the roots, is called "mull-madder."

From the madder-roots are also prepared by fermentation and filtration of the separated dye-colors the commercial extracts known as "madder flowers" and "guarancine." One hundred kilos. of madder will yield fifty-five to sixty kilos. of madder flowers.

The tinctorial value of the madder depends upon the existence of the two coloring matters, alizarin, $C_{14}H_8O_4$, and purpurin, $C_{14}H_8O_5$, both of which have been mentioned under the artificial dye-colors derived from anthracene. (See p. 420.) These are not found free in the growing plant, but combined as glucosides and other compounds easily decomposable by fermentation. As a nitrogenous and soluble ferment *erythrozym* is present; so soon as the solutions of madder extract are exposed to the air the *ruberythric acid* (or alizarin glucoside) is decomposed into alizarin and dextrose and the *pseudo-purpurin* (or naturally occurring purpurin-carboxylic acid) is decomposed into purpurin and carbon dioxide. Two other anthracene derivatives also occur in madder, both probably as decomposition products of pseudo-purpurin, *munjistin*, $C_{15}H_8O_6$, and *xanthopurpurin*, $C_{14}H_8O_4$ (the latter of which is isomeric with alizarin).

The importance of madder and madder preparations has almost entirely disappeared with the development of the artificial alizarin manufacture. The colors obtainable from alizarin, isopurpurin or anthrapurpurin, and flavopurpurin, which are the products of the synthetical methods, have almost entirely replaced those formerly obtained from madder.

4. *Safflower* (syn. *Safflor, Fleurs de Carthame*) consists of the dried flowers of the *Carthamus tinctorius*, a plant first grown in Egypt and the East Indies, but now grown in Asia Minor, Spain, Alsace, Austria, and Central Germany. The flowers are of a deep reddish-orange color, and contain, besides a yellow coloring matter of no technical value, *carthamin*, or *carthamic acid*, $C_{14}H_{16}O_7$, a red dye of considerable importance for silk- and cotton-dyeing. It forms from .3 to .6 per cent. of the weight of the flowers. "Safflower carmine" is a solution of the carthamin in soda, and "plate carthamine" is a pure preparation of the dye which has been dried in crusts upon glass or porcelain plates. The most important commercial varieties of safflower are the Egyptian, which is the richest in dye-color, the East Indian, the Spanish, and the German. Safflower comes from Spain and France, the production having amounted in recent years to 400,000 pounds. However, it is now almost entirely displaced from use as a dye by the artificial dyes.

5. *Orseille*, or *Archil* (syn. *Orséille, Persio, Cudbear*).—The various species of lichens, as *Rocella tinctoria* and *Rocella fuciformis* from Angola, Zanzibar, Ceylon, and Mozambique, as well as from the Azores and South American coast, contain a mixture of phenols, phenol-ethers, and phenol-acids, such as orcin (or orcinol), erythric, orcellinic and lecanoric (or diorcellinic) acids. These by the action of air and ammonia yield *orcëin*, contained in the orseille (archil) extract as a red dye, and on drying the extract the cudbear or persio as a reddish-violet powder.

Archil extract occurs in commerce in two forms, paste and liquor. The solid matter consists mainly of the impure orcëin in combination with ammonia. Its preparation will be referred to later. Cudbear (or Persio) differs mainly from the orseille extract in being free from all excess of ammonia and moisture and in being reduced to a fine powder. An illustration of the orseille-yielding lichens is given in Fig. 116 (see preceding page) in the lower left-hand figure.

6. *Cochineal* (syn. *Cochenille*) is the dried female insect *Coccus Cacti*, which lives and grows on the plants of the Cactus family, especially the "nopal," or *Cactus opuntia*. The nopal-plant is indigenous to Mexico, but is also cultivated largely in Central America, the Canary Islands, the Island of Teneriffe, Algeria, and the East Indies.

The commercial varieties of cochineal are known as the *silvery-gray* and the *black* cochineal. These varieties are apparently produced according to the method adopted for killing the insects when they are swept off the leaves of the nopal-plant. If killed by immersion in hot water or by steam they lose the whitish dust with which they are covered and constitute the black variety (*zaccatila*); if killed by dry heat in ovens this dust remains and they yield the silvery-gray variety (*blanco*.) This latter is considered the better, and is sometimes simulated by dusting the black variety with powdered talc, gypsum, barytes, or stearic acid. The natural gray powder is a variety of wax known as *coccerin*.

The coloring matter of the cochineal is *carminic acid*, $C_{17}H_{18}O_{10}$, and may amount to fifteen per cent. of the weight of the dried cochineal, although Liebermann states that the average is from nine to ten per cent. Carminic acid is a purple substance soluble in water and alcohol, but only slightly so in ether. Chlorine readily destroys the carminic acid and nascent hydrogen reduces it to a leuco body, which again becomes red on exposure to the air. Chemically it is a glucoside, being capable of decomposition into *carmine-red*, $C_{11}H_{12}O_7$, and a sugar, $C_6H_{10}O_5$.

Carminic acid dissolves in caustic alkalies with a beautiful red color, forms purple precipitates with barium, lime, lead, and copper, and a fine red lake with alumina. A decoction of cochineal behaves with reagents somewhat differently from a solution of the pure carminic acid owing to the presence of phosphates, tyrosine, etc. The addition of alum or stannic chloride to it yields the fine red pigment known as "cochineal carmine." This as well as other preparations from cochineal will be referred to again under products. (See p. 458.)

7. *Kermes* (syn. *Kermès, Alkermes*) is a corresponding substance to cochineal, and consists of the dried female insects *Coccus Ilicis*, which burrow under the epidermis of the leaves or young shoots of the kermes oak (*Quercus coccifera*), growing in the south of France, Spain, and Algeria. The coloring matter of the kermes insect has not been sufficiently investigated; it is said to be identical with that of cochineal. It is not used any longer in dyeing.

8. *Lac dye* (syn. *Färberlack*) is the product of the *Coccus Lacca*, an East Indian insect which lives on the branches of the fig and other trees. The female insects exude a resinous substance which encloses them and attaches them to the twig. This constitutes the "stick-lac" (see p. 98), which contains about ten per cent. of coloring matter. This latter may be obtained by treating the stick-lac with carbonate of soda. The coloring matter of lac dye has been studied by Schmidt, who terms it *laccainic* acid, $C_{16}H_{12}O_8$, and found it to be very similar to carminic acid in most of its reactions. Many writers consider the two to be identical.

*B.* YELLOW DYES.

1. *Old Fustic* (syn. *Gelbholz, Bois jaune*) is the trunk wood of *Morus tinctoria*, indigenous to the West Indies and South America. It is also yielded by the *Maclura tinctoria* and *Broussonetia tinctoria*. The wood is hard and compact and has a pale citron-yellow color. It contains two col-

oring principles, *morin*, or *moric acid*, $C_{15}H_{10}O_7$, which occurs in the wood combined with lime, and *maclurin*, or *moritannic acid*, $C_{13}H_{10}O_6$, both of which are yellow dyes and are contained in the commercial extract.

2. *Young Fustic* (syn. *Fisetholz, Bois de fustet*) is the bark-free wood of the *Rhus cotinus*, a variety of sumach growing in the Levant, Spain, Hungary, Tyrol, and Italy. The coloring matter is stated by Schmidt to occur as a soluble compound of *fustin* and tannic acid. This *fustin* is a glucoside, and is decomposed by dilute sulphuric acid into *fisetin*, $C_{15}H_{10}O_6$, and isodulcite. A decoction of young fustic gives a fine orange color with alkalies and bright orange precipitates with lime and baryta-water, stannous chloride and lead acetate. It also gives a fine orange color with alumina mordants.

3. *Quercitron* is the crushed or rasped bark of the *Quercus nigra* or *Quercus tinctoria*, indigenous to North America, and grown also in Germany and France. It forms a brownish-yellow powder, from which an extract is also made. The coloring principle is *quercitrin*, $C_{21}H_{22}O_{12}$, a glucoside, which is decomposed by dilute sulphuric acid into *quercitin*, $C_{15}H_{10}O_7$, and isodulcite. Besides quercitin, the bark contains *quercitannic acid*, $C_{17}H_{16}O_9$. Quercitin is difficultly soluble in water, but easily soluble in alkalies with golden-yellow color. "Flavine" is the commercial name of a preparation of quercitron obtained by acting upon the bark first with alkalies and treating this extract with sulphuric acid; it is a varying mixture of quercitrin, quercitin, and isodulcite, having some sixteen times the coloring power of the bark.

Flavine and quercitron bark are used chiefly for dyeing cottons and woollens with tin mordants.

4. *Persian Berries*, or *Avignon Berries* (syn. *Gelbbeeren, Graines jaunes*), are the dried fruit of different buckthorn (*Rhamnus*) species. The different commercial varieties are the Persian (from *Rhamnus amygdalinus* and *Rhamnus oleoïdus*), coming from Aleppo and Smyrna, regarded as the richest in dye-color and the best in use, the French, or Avignon (from *Rhamnus infectoria* and *Rhamnus saxatilis*), the Levantine, or Turkish (from *Rhamnus infectoria* and *Rhamnus saxatilis*), and the Spanish (from *Rhamnus saxatilis*) and the Hungarian (from *Rhamnus amygdalinus*, etc.).

The coloring matter of the Persian berries is called by Liebermann *xanthorhamnin*, or *chrysorhamnin*, and is a glucoside, yielding under the influence of dilute acids *rhamnetin*, $C_{16}H_{12}O_7$ (or methyl-quercetin, $C_{15}H\,O_7.CH_3$), and isodulcite. Persian berries are used for yellows on wool and cotton with alumina or tin mordants.

5. *Weld* (syn. *Wau, Gelbkraut, Gaude*) consists of the leaves and other parts of the *Reseda luteola*, a variety of mignonette. It is cultivated in almost all parts of Europe, notably in the south of France, Germany, and England. The coloring matter is known as *luteolin*, $C_{15}H_{10}O_6$, and forms yellow crystals of silky lustre, insoluble in water, soluble in alcohol. It dissolves in alkalies with deep yellow color. It is used especially in silk-dyeing.

6. *Annatto* (syn. *Orlean*, or *Roucou*) is prepared from the fleshy pulp of the seed-shells of the *Bixa orellana*, indigenous to the West Indies and South America, but cultivated also in the East Indies. The commercial annatto forms a soft reddish-yellow paste of buttery consistency, or sometimes it is dried in hard cakes. It contains two coloring matters, *bixin*, $C_{28}H_{34}O_5$, and *orellin*, the former of which—the more important—is a red dye and the latter a yellow. The bixin dissolves in alkalies with yellow color. It

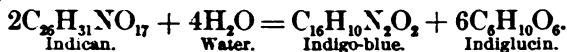
is used somewhat in silk-dyeing. Orellin is as yet only slightly studied, and is considered by some to be simply an oxidation product of bixin. By far the largest amount of annatto is used not in dyeing but in coloring butter and cheese. (See p. 270.)

7. *Turmeric* (syn. *Gelbwurz, Curcuma*) is the tuber of the *Curcuma tinctoria* and *Curcuma rotunda.* The roots are usually grayish-yellow on the exterior but deep yellow in the interior. The plant is indigenous to Central Asia. The varieties of it are the Chinese, Java, and Bengal, of which the latter is considered the best. The coloring principle is *curcumin,* $C_{14}H_{14}O_4$, which acts like a weak acid. The pure color is bright orange-red, but it dissolves in alkalies with a red-brown color. It is not employed alone as a dye-color, but is used in wool- and silk-dyeing for compound colors.

*C.* BLUE DYES.

1. *Indigo* (syn. *Indig-blau, Indigo*).—This is by far the most important of all the vegetable dyes. It has been known from very early times in the East, but was not introduced into Europe until the sixteenth century, where its use was at first prohibited because of the general culture of the woad, and indeed it was only in 1737 that its employment was legally permitted in France. However, in time it displaced the woad almost entirely, so that the latter is used now only in a few special cases.

The indigo-plant is an *Indigofera,* the more important varieties of which are the *Indigofera tinctoria,* cultivated in India, particularly in Bengal, Coromandel, Madras, Java, and Manila; the *Indigofera Anil,* cultivated in Guatemala, Caracas, Brazil, and the Antilles; the *Indigofera Argentea,* cultivated in Egypt, Senegal, and the Isle of France. Of lesser importance are the *Indigofera disperma* and the *Indigofera pseudotinctoria,* both cultivated in the East Indies. The *Indigofera tinctoria* is shown in Fig. 116 (see p. 442) to the left of the illustration above. The indigo dye does not exist as such in the plant but as the result of fermentation, whereby the naturally occurring *indican,* a glucoside, is decomposed, most probably according to the reaction:

$$\underset{\text{Indican.}}{2C_{26}H_{31}NO_{17}} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Indigo-blue.}}{C_{16}H_{10}N_2O_2} + \underset{\text{Indiglucin.}}{6C_6H_{10}O_6}.$$

The plants are cut at two or three different periods in the year when they have just come into bloom. They are at once packed into bundles and put into the soaking-vats covered with water. A fermentation here ensues, which is completed in from ten to eighteen hours, according to the temperature of the air and the ripeness of the plants. When the supernatant liquid has taken a yellowish-green color and has a pleasant sweetish taste, the fermentation is stopped and the liquid is run off into vats placed at a lower level. Here it is beaten vigorously with sticks or paddles for from one and a half to three hours by men who enter the vats for the purpose. The liquid is changed by this treatment to a deep-blue color and becomes covered with froth of like color. When the men leave the vat to rest, the separated indigo rapidly settles, and in some two to three hours the supernatant liquid can be run off from stopcocks placed in the side of the vat at levels above the indigo precipitate. Milk of lime is often added to hasten the settling of the separated indigo, and more recently dilute ammonia has been used. The addition of this latter reagent is said to increase the yield of indigo and to improve its quality, as it contains less indigo-brown and resinous impurities. The thin paste of indigo and water is then drawn off, boiled to prevent subsequent fermentation, and strained through a sheet. It is

then put into square press-boxes lined with cloth and provided with holes in the sides and bottom for thorough drainage of the indigo. Pressure is then applied, gentle at first but stronger as the indigo hardens and acquires a firmer consistency. The mass is then cut into cubical blocks, which are stamped with the name of the factory and put on shelves in the drying-house to slowly dry out, great care being taken to avoid drafts of air, which might cause the cakes to crack in drying. Three hundred kilos. of indigo-plants yield an average of one kilo. of indigo. The commercial product contains from twenty to eighty per cent. of the indigo-blue (averaging about forty-five per cent.), and with this two other coloring matters, indigo-brown and indigo-red, besides indigo-gluten, moisture, and a variable amount of mineral matter.

The commercial varieties of indigo are, first, the Asiatic, of which the Bengal indigo is the best, followed by the Java, Madras, Coromandel, and Manila varieties; second, the American, of which the Guatemala is the best, followed by the Caracas and the Brazilian varieties; and, third, the African, including the Egyptian, Senegal, and Isle de France varieties.

Indigo-blue is insoluble in water, alcohol, ether, dilute acids, and alkalies, soluble in fuming sulphuric acid, aniline, nitrobenzene, chloroform, and glacial acetic acid. It may be sublimed by heat, although with partial decomposition when the sublimation is carried out at ordinary atmospheric pressure. By the action of alkaline reducing agents it is changed to indigo-white, $C_{16}H_{12}N_2O_2$, and dissolved. Upon this reaction and the subsequent change of the indigo white when deposited upon the textile fibre, by atmospheric oxidation back again into indigo-blue, is based the use of indigo in vat-dyeing. (See p. 484.) Indigo is used on the most extensive scale for cotton- and wool-dyeing, less generally for silk.

2. *Woad* (syn. *Waid*, *Pastel*).—The leaves of the *Isatis tinctoria* and *Isatis lusitanica* moistened, slightly fermented, and then compacted and dried into balls constitute the woad of commerce and furnish an additional source of indigo. As before stated, the use of the woad for dyeing antedated the use of the indigo-plant, and the cultivators of the woad, particularly in Central Germany, long fought against the introduction of the richer tropical indigo-yielding material, but in vain. The woad-culture is still carried on in different parts of Europe, particularly in France and Germany, but in small degree compared with its former development. The woad contains only .3 per cent. of indigo reckoned on the weight of the fresh leaves, or as it is often calculated, one hundred kilos. of woad have the same coloring power as two kilos. of indigo. The woad balls improve in quality by keeping for some years, the best variety coming from the south of France under the name of Pastel. The woad is rarely used by itself in dyeing operations, but along with indigo as a means of inciting the fermentation in the "woad-vat" process of dyeing.

A few other plants, such as *Polygonum tinctorium*, indigenous to China, and *Eupatorium tinctorium*, indigenous to Brazil, have been found to contain indigo, and have been used locally for blue-dyeing.

3. *Logwood* (syn. *Blauholz*, *Bois de Campêche*).—This is the heartwood, freed from bark and sap-wood, of the *Hæmatoxylon Campechianum*, a tree indigenous to Campeachy Bay, Central America, but grown now in various parts of Central and South America and the West Indies. The commercial varieties are the Campeachy, Yucatan, Laguna, Honduras,

Jamaica, St. Domingo, Monte Christo, Fort Liberté, Martinique, and Guadeloupe logwoods.

Of these, the first commands the highest price on account of the large yield of coloring matter obtainable from it and the readiness with which it "bronzes" when submitted to the "curing" process. The wood comes in logs or sticks of smaller size, and is then chipped or rasped by the makers of extracts, who sell it in the chipped or rasped condition as well as in the form of prepared extract. The wood has a dark-red color on the exterior but is yellowish-red in the interior, has a weak odor of violets and a peculiar sweetish but astringent taste. On moistening the wood or chips with ammonia it takes a dark-violet color. Logwood contains some nine to twelve per cent. of the chromogen, *hæmatoxylin*, $C_{16}H_{14}O_6$, which is present in the wood partly in the free state but mainly as glucoside. It forms colorless prismatic crystals difficultly soluble in water, easily soluble in alcohol and ether. From the hæmatoxylin by oxidation in the presence of alkalies, and particularly ammonia, is produced *hæmatëin*, $C_{16}H_{12}O_6$, the true dye-color. This forms small crystals or crystalline scales of dark-red color and greenish metallic lustre, which show plainly upon the wood, especially after the fermentation or curing. It is difficultly soluble in water, alcohol, and ether. Hæmatëin forms a crystalline compound with ammonia, $C_{16}H_{11}(NH_4)O_6 + H_2O$, which, however, is decomposed by acids or by heating to 130° C., leaving pure hæmatëin. Zinc and sulphuric acid readily reduce the hæmatëin to hæmatoxylin again. Logwood is used on an extended scale in dyeing wool, silk, cotton, and leather. It is used for deep blues, blacks, and jointly with other coloring matters for composite shades of color.

4. *Litmus* (syn. *Lakmus*, *Tournesol*).—This is a dyestuff very similar in character to orseille and persio (see p. 443), and also derived from the class of lichens. For its preparation the same lichens may be used, although at present the different species of *Lecanora* serve as the chief material, such as *Lecanora orcina*, *L. dealbata*, *L. parella*, which occur in the French Pyrenees, and the *Lecanora tartarea*, occurring in Iceland and Scandinavia. The lichens are allowed to ferment after the addition of stale urine or ammonia and carbonate of potash. When the mass has assumed a deep-blue color, chalk or gypsum are added, and it is shaped into small cubes and dried. The coloring matter is *azolitmin*, $C_7H_7NO_4$, which differs by one atom of oxygen only from the orcëin of orseille extract, $C_7H_7NO_3$. It acts like a weak acid, the salts of which are blue in color (the potassium compound existing in the commercial litmus), and which when set free by acids is reddish in color.

*D.* GREEN DYES.

We have practically nothing here that has assumed practical value as yet. The only ones needing mention at all are:

1. *Chlorophyll.*—This is the green coloring matter of fresh vegetation, and is abundantly present in nature, but it has not been found possible hitherto to isolate it in a pure state adapted for use. Schütz has, however, separated it from the yellow coloring matter accompanying it, *xanthophyll*. It is stated that chlorophyll forms a beautiful green color with zinc as mordant which is adapted for dyeing, but it has not as yet been used in practice.

2. *Lokao, or Chinese Green*, is a green pulverulent deposit from the decoction of the bark of *Rhamnus chlorophorus* and *Rhamnus utilis*, both indigenous to China. Kayser, who has investigated the lokao, states that the coloring matter is *lokaonic acid*, $C_{42}H_{48}O_{27}$, which is combined in the

commercial preparation as the alumina lake. This lokaonic acid is decomposed by acids into *lokanic acid*, $C_{36}H_{36}O_{21}$, and *lokaose*, an inactive sugar. Lokao has been used for cotton- and silk-dyeing, but is practically displaced by the cheaper artificial colors.

*E.* BROWN DYES.

1. *Catechu* (or *Cutch*).—This has already been spoken of as one of the raw materials of the tanning industry. (See p. 322.) It finds, however, an equally extended use in dyeing as an adjective color. The explanation of this is that catechu contains two principles, *catechin*, $C_{21}H_{20}O_9 + 5H_2O$, a yellow dye forming brown precipitates with copper, alumina, and tin mordants, and *catechutannic acid*, $C_{13}H_{12}O_5$. The former is present in amount from twenty to thirty per cent., the latter, however, from forty-eight to fifty-two per cent. The best variety of catechu is the Pegu catechu, and after this the Bombay and the Bengal catechu. Catechu is extensively used in both cotton- and silk-dyeing for browns and for composite shades.

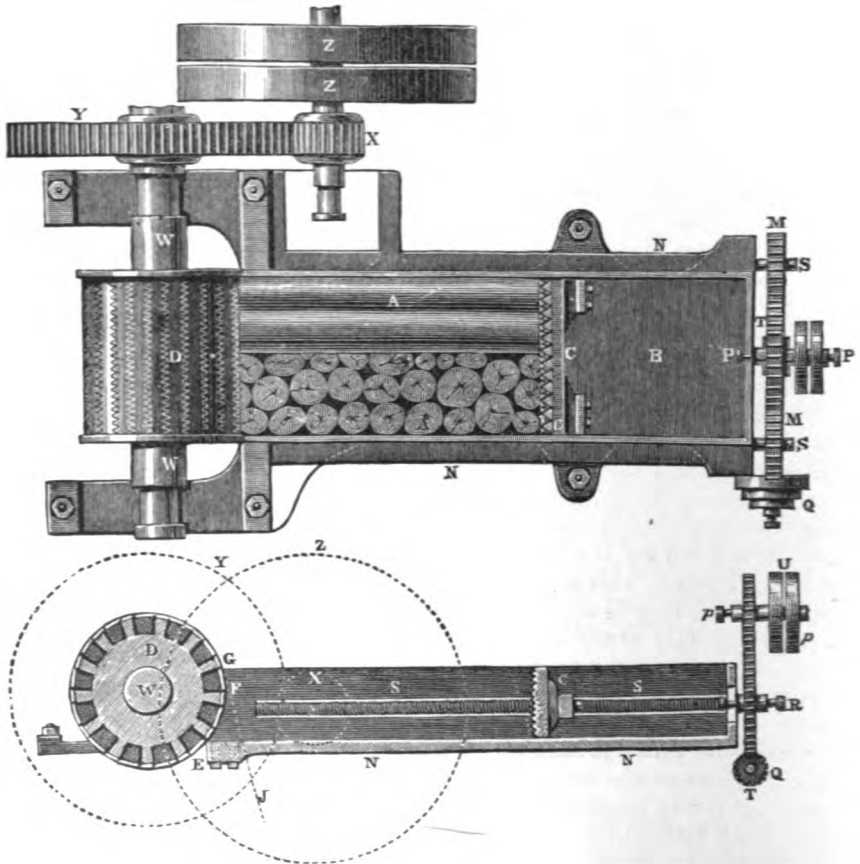
2. *Kino* is a natural dyestuff very similar to catechu and comes from a variety of sources, as *Butea frondosa* and *Butea superba*, yielding the Bengal kino ; *Pterocarpus erinaceus*, yielding the West African kino ; *Eucalyptus corymbosa* and other Eucalyptus species yielding the Australian kino. The important principles are *kinöin*, $C_{14}H_{12}O_6$, and its anhydride, *kino-red*, $C_{28}H_{22}O_{11}$. It is used like catechu for dyeing.

## II. Processes of Treatment.

1. CUTTING OF DYE-WOODS.—Whether the dye-woods are to be used for the manufacture of extracts or used as wood by the dyer, they must be reduced to powder or cut into chips of small size. This process varies with different manufacturers. In America, it is usually one of cutting with powerful knives, in which whole logs are brought with their ends against rapidly-revolving cylinders, on the circumference of which are heavy steel knives, which cut off flat chips directly across the grain about one-eighth inch in thickness. This method is a very rapid one, as but little previous splitting of the logs is necessary. In Europe, where labor is cheaper, the logs are frequently sawed and split into billets about two feet long and two to three inches in thickness, and these are then brought by hand diagonally against toothed knives on a rapidly-revolving cylinder, by which means the wood is torn or rasped into a much finer condition, or these billets are put into a machine which presses them in this way against the revolving knives. Such a machine of German design is shown in Fig. 117, where a rotating drum, *D*, carrying on its circumference a series of knife-blades, is continuously cutting the billets of wood which are pressed against it.

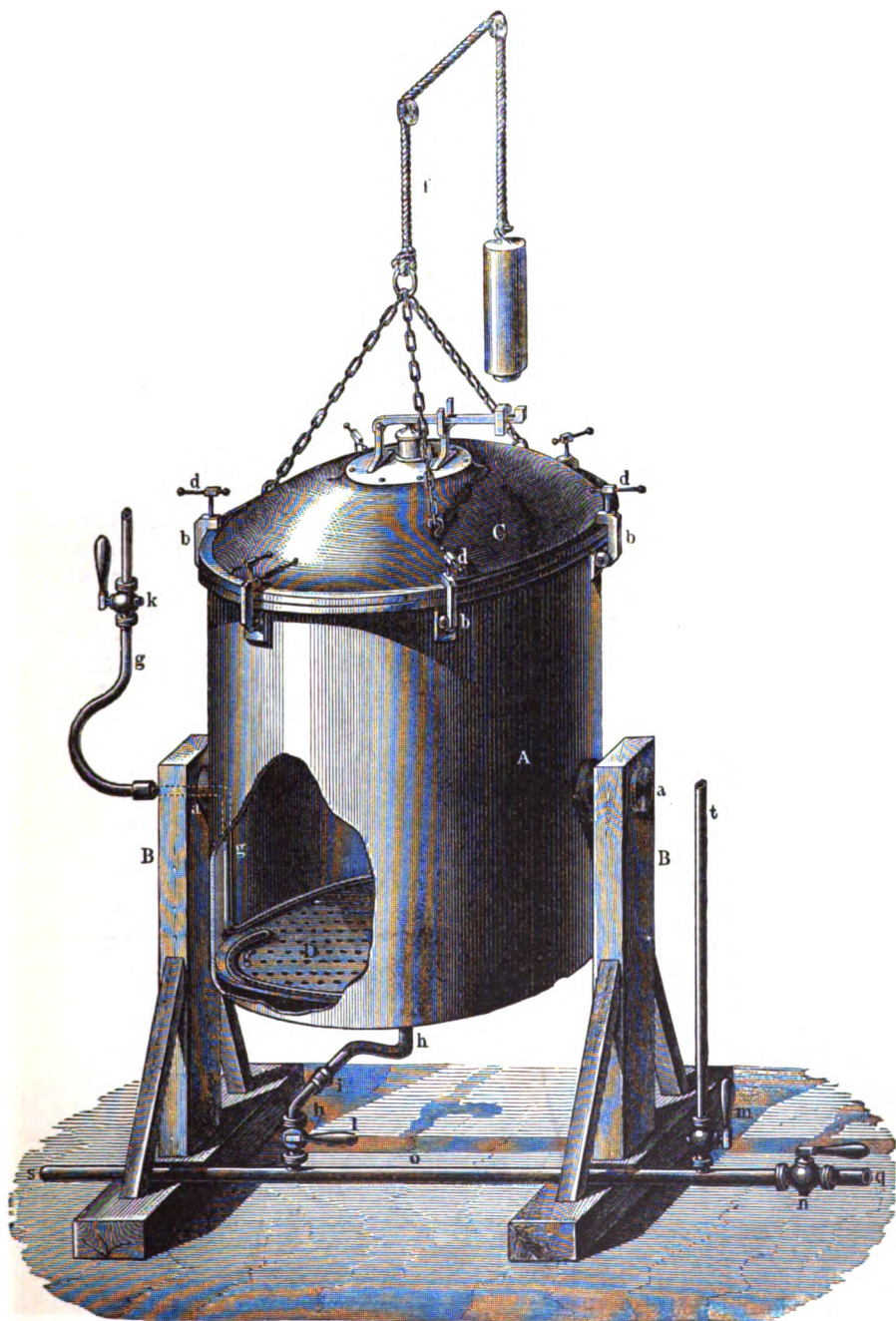
2. FERMENTATION OR CURING OF DYE-WOODS.—As has already been stated in several cases, the dye-woods in the fresh condition contain not the finished dye-color, but a chromogen capable of passing into the former under the influence of oxidizing or other agents. Notably is this the case with logwood, and the chips or rasped wood are therefore submitted to a curing treatment by moistening them with water and exposing them to the air in heaps some three feet in depth for from four to six weeks. The chips heat up, and the pile must then be turned with shovels to regulate the temperature and allow contact with the air. More water is then added, and the process continued until the chips assume a rich reddish-brown color or become coated with a bronze powder (hæmatëin). Various chemicals

have been suggested to hasten the operation, such as ammonium carbonate and chloride, stale urine, sodium carbonate, potassium nitrate, chalk, and glue. None of these are known certainly to be of benefit. The alkalies give the chips a fine red color at first, but unless great care is taken they cause them to become black from over-oxidation before the action can be checked. Glue has been used because it is said to combine with the tannin of the wood, and by removing it to open up the pores of the wood to the oxidizing influence and so facilitate the curing. But the existence of tannin in logwood has not been at all certainly established.

Fig. 117.

Curing is of value to the dyer because it enables him to rapidly obtain the color from the chips and gives him a liquor containing a more highly oxidized coloring matter, which "goes on" the goods more rapidly. It must be remembered, however, that curing the chips enables the manufacturer to sell twenty to thirty per cent. of water with them, while uncured chips contain ten to fifteen per cent. of moisture.

When the chipped logwood is intended for the manufacture of extract it is usually conveyed directly to the extractors without curing, which is, no doubt, the better procedure, since all oxidation in the first part of the process objectionable.

3. Manufacture of Dye-wood Extracts.—As dye-woods contain generally only a tenth or less of their weight of dye-color, it becomes a

Fig. 118.

matter of great economy in transportation and storage to prepare from them extracts, either as concentrated liquids or solids representing the active coloring principle. This is done by manufacturers who make a specialty of this extracting, and apply to it the best designed and most improved machinery.

The operation may be divided into two stages,—the extraction and the concentration. For extraction a rasped wood such as is made in France has many advantages over the chipped, since it yields its coloring to a smaller quantity of water and at a lower temperature than the chips. The extraction consists in heating the wood with water under various conditions and then drawing off the liquor into tanks for settling or treatment. The conditions refer to the kind of vessels, the amount and quality of the water, and the temperature. Many European manufacturers use open wooden vessels for extractors, so that the temperature does not get above 100° C. As this method was first used in France, it is known as the French process. The use of closed extractors, however, allows of increase in the pressure, and this within limits much facilitates the perfect extraction. A closed extractor of German design, in which a pressure not exceeding two atmospheres is used, is shown in Fig. 118. (See preceding page.) It will be seen that the vessel, *A*, is provided with a false bottom, *D*, to allow of the draining off the extract liquor, a perforated steam-pipe, *g*, to rapidly bring up the contents of the extractor to the required temperature, and a drainage-pipe, *h*, to draw off the thin extraction liquors.

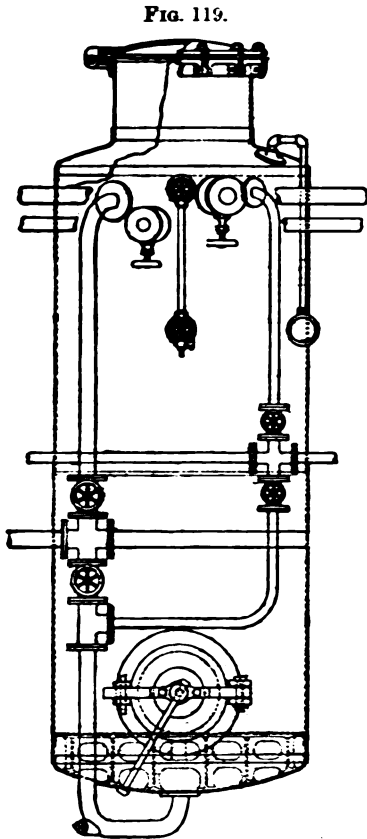
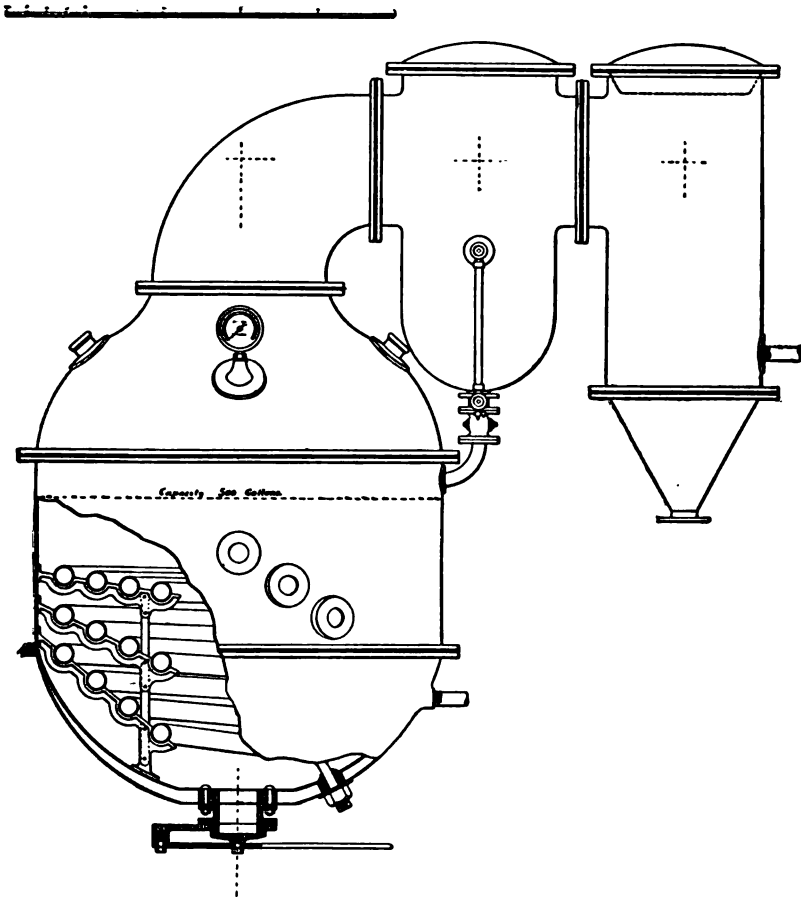



FIG. 119.

In America closed copper or iron vessels are used, arranged in battery form very much like the diffusion apparatus now used in the extraction of sugar. One cell of such an extraction battery is shown in Fig. 119. This method allows of continuous working, as one cell of the series can be emptied of exhausted dye-wood and loaded with fresh chips while the extraction liquors are passing successively through the other cells of the battery and acquiring the maximum strength. The temperature or pressure varies with different manufacturers, but most writers on the subject agree that a pressure not exceeding fifteen to twenty pounds excess over atmospheric pressure should be used. An increase in the pressure is always attended with an increase in the yield, and after a certain point with a decrease in the coloring value of the resulting extract. When the liquors from the extractors are run into large tanks and allowed to cool much wood-fibre and some resinous matter separates. The clear liquor is then drawn to the evaporators, which in this country almost invariably consist of

vacuum-pans, but in Europe often consist of open pans or vessels in which heated disks revolve so as to favor the evaporation. While the liquor is still thin, double- or triple-effect pans are used, and of recent years the Yaryan evaporators (see Fig. 40, p. 131) have been applied with great success to the evaporation of dye-wood extracts. As the liquors become thicker the concentration is continued in vacuum-pans more analogous to the strike-pans of the sugar refinery. Such a vacuum-pan designed for use in the manufacture of dye-wood extracts is shown in Fig. 120. When the gravity

Fig. 120.

of the liquid becomes 42° or 51° Tw., it is drawn off into barrels for shipment, or if the solid extract is desired the concentration is continued in a vacuum-pan.

Various methods of treatment have been suggested at different stages of the process with a view of improving the extract, but it is an open question whether anything better than pure water has yet been used. The addition of solutions of glue and of different salts to the wood before extraction has been frequently recommended. Chalk suspended in water and dilute lime-

water have also been recommended to be similarly used. Such processes could only result in an over-oxidized product. Borax has also been used, but without notable advantage in the case of logwood, although it serves very well in the case of the redwoods. The use of chlorine, hypochlorites, and chlorates has been patented in connection with logwood extract for addition either to the wood or the liquor after extraction, but it is doubtful if any of these are used on a large scale at the present time. That these substances and many others develop the color of logwood there can be no question, but to be of value to the dyer that development must take place in the presence of the goods.

The yield of logwood extract by the American process of manufacture is said by Soxhlet * to be twenty or twenty-one per cent. of solid extract, while that by the French process is sixteen and a half per cent. The latter is superior in quality, and is therefore almost invariably reduced by the addition of such substances as molasses, glucose, and extract of chestnut. In America, in addition to the above, extract of hemlock and extract of quercitron (after the removal of the flavine) are considerably used to adulterate logwood extract.

4. MISCELLANEOUS PROCESSES.—(*a*) *Preparation of Guarancine and Madder Flowers.*—For the preparation of guarancine, the pulverized madder-root is warmed gently with dilute sulphuric acid (one part acid and two parts water) for some time, whereby the glucosides of the madder are decomposed. The sugary liquid is drained off and the residue heated with concentrated sulphuric acid, which decomposes the woody fibre and other organic substances present and decomposes any lime compounds that may have been in the madder. The whole mixture is now thrown into water, the precipitate collected, washed, and dried. The guarancine now contains the alizarin and purpurin in uncombined form. The yield is from thirty-four to thirty-seven per cent. For the preparation of "madder flowers" the powdered madder is set to ferment with warm water to which a little dilute sulphuric acid had been added. After some days, the liquid is filtered and the residue washed, pressed, and dried. The flowers of madder can be used more readily than crude madder in dyeing at low temperatures, and give finer and purer violets.

(*b*) *Preparation of Ammoniacal Cochineal and Carmine.*—Five parts of powdered cochineal are mixed with fifteen parts of ammonia-water, and the mixture is allowed to stand in a warm place with frequent stirring for some four weeks. Some two parts of alumina are then added, and the mixture carefully evaporated in a porcelain dish until the odor of ammonia has disappeared. The preparation so obtained, known as ammoniacal cochineal, yields its color more readily than cochineal and produces brighter shades of color.

Cochineal-carmine is a brilliant red pigment prepared from decoction of cochineal by the action of alum under certain conditions. The details of its preparation vary and are kept by different manufacturers as trade secrets. The following process has been published:† Five hundred grammes of finely-powdered cochineal are boiled for one-quarter of an hour with thirty times the weight of distilled water, thirty grammes of acid tartrate of potassium added, boiled for ten minutes longer, fifteen grammes of alum added and boiled for two minutes longer. The clear liquid is allowed to stand in shal-

* Textile Colorist, xiii. p. 125.

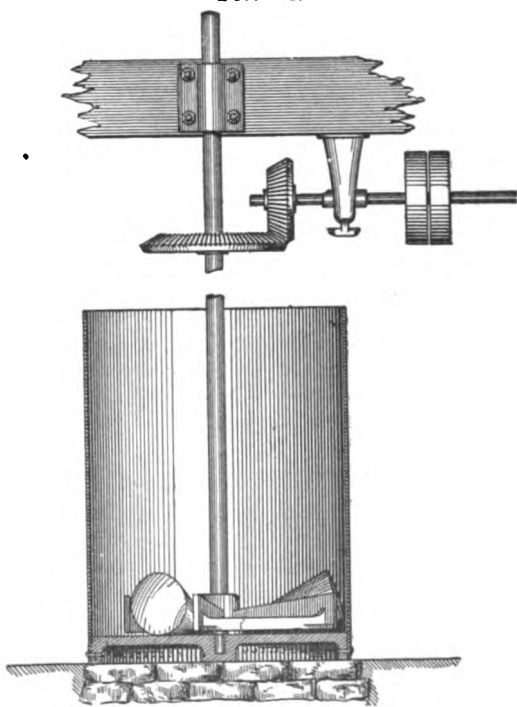
† Schützenberger, Die Färbstoffe, ii. p. 338.

low glass vessels, when the carmine separates in a very fine state. It is washed with water and dried in the shade. Or, by another process,* one pound of cochineal and one-half ounce of potassium carbonate are boiled with seven gallons of water for fifteen minutes. The heat having been withdrawn, one ounce of powdered alum is added, and the liquid stirred and allowed to settle. The clear liquid is decanted, one-half ounce of isinglass added, and heat applied until a coagulum forms, when the liquid is briskly stirred and allowed to settle.

(*c*) *Preparation of Flavine.*—As stated before (see p. 445), flavine is a preparation containing the coloring matter of the quercitron bark in purer and more concentrated form. The method for its preparation is not generally known, although it is found to contain quercetin as well as quercitrin, and frequently the former in larger amount.

A procedure that has been published † is the following: Two hundred and fifty kilos. of the powdered quercitron are boiled for fifteen minutes with fifteen kilos. of crystallized soda and two hundred kilos. of water, there is then added to the liquid sixty-one kilos. of sulphuric acid of 66° B., and the boiling continued for three-quarters of an hour longer, when the whole is allowed to cool and settle, the liquid poured off, and the separated color drained and dried.

(*d*) *Preparation of Indigo-carmine, Soluble Indigo, etc.*—It was stated in an earlier section (see p. 447) that indigo-blue was soluble in strong sulphuric acid. The solubility depends, however, upon the chemical action of the acid, whereby sulphonic acids of indigo are formed. Two such acids, indigo-monosulphonic acid (sulpho-purpuric acid), $C_{16}H_9(HSO_3)N_2O_2$, and indigo-disulphonic acid (sulphindigotic acid), $C_{16}H_8(HSO_3)_2N_2O_2$, are formed. Of these, the first is insoluble in water or dilute acids, while the second is soluble with deep-blue color. Both are formed together in practice when indigo is dissolved in strong sulphuric acid, although if not more than four parts of sulphuric acid to one of indigo be used and too prolonged heating be avoided, the monosulphonic acid will be formed predominantly, while if some fifteen parts of ordinary concentrated sulphuric acid or seven parts of fuming

FIG. 121.

* Allen, Commercial Organic Analysis, 2d ed., iii. p. 367.

† Gerb- und Farbstoffe-Extracte, Mierzinski, p. 208.

sulphuric acid be taken to one of indigo and the heating be continued, the disulphonic acid will be the sole product. After treatment with the acid the dissolved mass of indigo is allowed to cool down and then strained to remove any lumps that may have escaped grinding; salt is thrown in, which precipitates the indigo-sulphonic acids, which are removed by filtration through felt. For finer grades of "indigo extract" the precipitate is redissolved in water and reprecipitated with salt several times, each precipitation removing a greater quantity of the objectionable green coloring-matter. Whatever be the process or proportion of acid used, the indigo must be very finely ground. This is done in indigo-mills, which are of various forms, known as "ball-mills," in which rotating cannon-balls gradually grind the color, as "cylinder-mills," in which heavy iron rolls accomplish the same work, and other forms. An illustration of such an indigo-mill with conical rolls, taken from a form in current use, is shown in Fig. 121. The direct use for dyeing of the product obtained by the action of sulphuric acid upon indigo is no longer common. The preparation and sale by the color manufacturers of pure preparations, known as *Indigo Extract*, *Soluble Indigo*, or *Indigo-carmine*, has replaced them. The sodium salt of the monosulphonic acid constitutes "indigo-purple" or "red indigo-carmine," the sodium salt of the disulphonic acid the true "indigo-carmine," which comes into commerce in paste form under that name or as a dry powder known as "Indigotin."

This indigo-disulphonic acid fixes itself on the animal fibre like other acid dye-colors, and hence "indigo-carmine" has an extended use in wool-dyeing. The wool is generally mordanted with alum and then dyed in an acid bath containing sulphuric acid.

## III. Products.

1. From Red Dyestuffs.—(*a*) *Brazil-wood Extracts* are made by the diffusion process, three varieties coming into commerce,—a liquid extract of 20° B., a liquid one of 30° B., and a solid one. One kilo. of the dry extract corresponds on the average to twelve kilos. of the wood. *Brasilin* is also manufactured on a large scale almost pure by Geigy, of Basle.

This brasilin often separates in the form of a crystalline crust on the surface of the commercial extract liquors. These crusts contain the brasilin mixed with the lime compound of the same. If this crude product is boiled with very dilute alcohol with the addition of zinc dust and hydrochloric acid and the solution stood aside to crystallize a very pure product is obtained.

Brasilin is relatively easily soluble in water, alcohol, and ether. In alkalies it is soluble with carmine-red color. Zinc dust will decolorize the solution, but on exposure to the air it speedily takes up the red color again. Acetate of lead precipitates a colorless crystalline compound which gradually turns red. Brasilëin bears the same relation to brasilin that hæmatëin bears to hæmatoxylin, and can be prepared by the oxidation of the alkaline solution of brasilin in the air.

Brazil-wood extracts are used in wool- and cotton-dyeing. With alumina mordants they produce shades resembling the alizarin lakes, but inferior in character. On wool mordanted with bichromate of potash they produce a fine brown.

The insolubility of the coloring matters in sandal-wood prevents their being used in the form of extracts.

(*b*) *Madder Preparations.*—We have already referred to *Guarancine* and *Flowers of Madder*. *Guaranceux* is the name applied to the impure purpurin recovered from the sediment of the waste-liquors in madder-dyeing.

*Pincoffin* (*Alizarine commerciale*) is a preparation from guarancine, in which the purpurin has been decomposed by superheated steam, leaving the alizarin unchanged. It has twenty-five per cent. less coloring power than the guarancine, but gives finer violets than can be obtained with the former.

(*c*) *Safflower Preparations.*—These are practically more or less pure preparations of carthamin, and the names *Safflower Extract*, *Safflower-carmine*, *Safflower-red*, and *Plate-red* refer to different concentrations of the carthamin solution. For the preparation of the pure safflower-red, the safflower-yellow must be removed by washing the crushed flowers with water until this runs off colorless. The residue is then treated with water and fifteen per cent. of its weight of crystallized soda salt. The solution is strained from the residue, filtered, and after acidulating with acetic or citric acid, cotton yarn is immersed in it to take up the color. The dyed cotton is stripped of the color by a five per cent. soda solution, and from this solution the color is again precipitated by citric acid. It is now drained, and comes into commerce as a paste known as "Safflower Extract." The color must be kept in sealed flasks, protected from the light. This paste dried upon plates at a gentle heat yields the so-called "plate-red." It then forms a red powder with greenish reflex, almost insoluble in water and ether, but easily soluble in alcohol. It is also soluble in alkalies with yellowish-red color. The "safflower-carmine," on the other hand, is prepared from the extract paste by washing the insoluble color and dissolving it in alcohol, which is then left to slowly evaporate. For dyeing purposes the safflower-carmine is dissolved by addition of soda, and the bath is then made slightly acid with citric acid; or the soda-extraction liquors from the flowers, which have been washed with water, may be used directly, acidifying the bath as before. Safflower-red is fixed in a weak acid bath both upon the animal fibre and upon the unmordanted cotton. On silk it produces a fine rose-red color.

(*d*) *Orseille Preparations.*—These come into commerce both as paste and liquor. The solid matter consists essentially of the impure orcëin in combination with ammonia. It is liable to be adulterated with the spent weeds from the manufacture of the orseille liquor or with other vegetable coloring matters. It is also at times adulterated with aniline dyes, such as magenta, acid magenta, and methyl violet. Various azo dyes, producing colors ranging from crimson to claret-red, are now sold as substitutes for the orseille extract, and, being cheaper, are used to adulterate it. These are known as "orchil extract," "orchil-red," "orselline," etc. They may be detected when so admixed by their behavior with salt solution and basic acetate of lead. The liquid extract is usually brought to 25° B., and is frequently adulterated with logwood or Brazil-wood extract. *Orseille Purple* (French Purple) is a pure orseille dye, obtained by extraction of the lichens with a fifteen per cent. ammonia solution, precipitation with hydrochloric or sulphuric acid, and redissolving in ammonia. This solution is then left exposed to the air in shallow vessels until it becomes dark purplish-violet. The color is then precipitated by addition of sulphuric acid, washed, and dried. *Orseille Carmine* is a similar preparation, in which the ammoniacal solution, after exposure to the air until it becomes cherry-red, is heated

with alum or calcium chloride. *Cudbear*, or *Perseo*, as before stated, is a dry powder obtained by evaporation of the extract, or prepared direct from the lichens by the action of ammonia or urine and then evaporated to the condition of a powder. It is often adulterated with common salt and other mineral matters, and is liable to much the same organic impurities or adulterants as orseille.

(*e*) *Cochineal Preparations.*—Ammoniacal cochineal and cochineal-carmine have already been referred to. *Ammoniacal Cochineal* is distinguished from carminic acid by giving a purple or violet precipitate (instead of scarlet) with oxymuriate of tin. The crimson, purple, and mauve colors it yields with mordants are not affected by acids so readily as those produced directly by cochineal. Ammoniacal cochineal is used in admixture with ordinary cochineal for producing the bluer shades of pink. *Cochineal-carmine* requires for its production a decoction of cochineal itself and not of carminic acid, the nitrogenized matters being essential to its formation. Liebermann,* who has investigated carefully the nature of the cochineal coloring matter, found it to contain 3.7 per cent. of nitrogen, of which only .25 per cent. could be expelled by boiling with dilute alkali, the remainder existing apparently as proteïds. He gives the following as the composition of the commercial sample of carmine examined by him: Water, seventeen per cent.; nitrogenous matter, twenty per cent.; ash, seven per cent.; coloring matter, fifty-six per cent.; wax, traces. Liebermann considers cochineal-carmine to be no ordinary compound of a coloring matter with alumina, but as an alumina-albuminate of the carmine coloring matter, comparable in some respects to the product from alizarin and alumina with "Turkey-red oil." Carmine forms red, porous, relatively light masses, which are easily rubbed up to a fine red powder. It is insoluble in water and alcohol, but readily soluble, when pure, in aqueous ammonia. Cochineal-carmine is liable to adulteration with starch, kaolin, vermilion, red-lead, chrome-red, etc. These admixtures may be detected by treating the sample with dilute ammonia, in which a pure sample should be completely and readily soluble.

M. Dechan † has published a series of analyses of commercial carmine, which are here given:

| | | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Moisture | | 22.1 | 16.1 | 2.0 | 22.3 | 20.2 | 23.5 | 8.5 | 10.0 | 21.2 | 13.0 |
| Soluble in ether. | Coloring matter | 46.1 | 69.2 | 34.1 | 65.7 | 60.8 | 69.5 | 26.1 | 72.0 | 18.4 | 67.5 |
| | Alumina, lime, etc. | 8.0 | 9.8 | 11.4 | 12.0 | 9.0 | 7.0 | 0.4 | 8.1 | 4.4 | 10.0 |
| Soluble in ether. | Organic matter | 21.8 | 2.5 | 18.5 | ... | 9.8 | ... | .. | 8.0 | 52.4 | 9.5 |
| | Ash | 2.0 | 2.4 | 34.0 | Trace. | 0.2 | Trace. | 14.6 | 1.9 | 3.6 | Trace. |
| | Vermilion | ... | ... | ... | ... | ... | ... | 50.4 | ... | ... | ... |

Cochineal is not used in cotton-dyeing. In dyeing silk it has also been almost entirely superseded by aniline reds, and in wool-dyeing the azo colors have to a great extent replaced it. Two distinct shades of red are obtained with cochineal, according to the mordant used,—*cochineal-crimson* with cream of tartar and alum, and *cochineal-scarlet* with stannous chloride and cream of tartar or oxalic acid.

2. From Yellow Dyestuffs.—(*a*) *Old Fustic Extracts.*—Both a liquid extract of about 20° B. and a solid extract have been prepared. The

* Ber. Chem. Ges., xviii. p. 1971. † Pharm. Journ. [3], xvi. p. 511.

latter forms large yellowish-brown blocks of a waxy lustre, which dissolve in water with yellow color. They are prepared from the wood by diffusion. The name *morin* has been given to a commercial product obtained by boiling the rasped wood with a two per cent. soda solution and evaporating the solution so obtained to a specific gravity of 1.041, when on cooling the morin and moritannic acid separate out.

(*b*) *Quercitron Extracts, etc.*—Both liquid and solid extracts are used commercially. The former of 20° and 30° B. respectively, and the latter as a dark-brown mass of waxy lustre. The extracts contain, as a rule, mixtures of quercitrin and quercetin. *Flavine* has already been referred to. It is a preparation in which the quercitrin of the bark has been extracted and in large part changed by subsequent treatment with sulphuric acid into quercetin, which is superior in coloring power. The tannic acid of the bark extract has also been removed and the lime salts, so that it gives much purer colors than the original extract. Flavine is largely used in connection with cochineal or lac-dye for producing scarlet. A quercitron extract to which stannite of soda or sulphate of zinc has been added is said to be used under the name of "Fustic Substitute." It can be told from genuine extract of fustic by the test with ferric chloride, which produces a brown precipitate, turning olive-green with fustic, but a greenish-black with quercitron extract.

(*c*) *Persian Berries.*—A thick extract is prepared from Persian berries, soluble in water with yellow color shading into brown. The solution becomes clearer on addition of hydrochloric or nitric acids and deposits a dirty yellow precipitate. Ammonia or caustic soda color it a reddish-yellow, stannous chloride gives at once, and stannic chloride after the addition of carbonate of soda, a golden-yellow precipitate, iron salts a dark olive-green to greenish-black color.

3. From Blue Dyestuffs.—(*a*) *Commercial Indigo* occurs in lumps or fragments of a deep-blue color, usually showing a bronze or purple-red streak when rubbed with any hard substance, or in the case of the better kinds with the friction of the thumb only. The fracture of indigo is dull and earthy, it sticks to the tongue, is odorless and tasteless. The specific gravity varies from 1.324 to 1.455. Helen Cooley * has given the following determinations of indigotin, ash, and specific gravity in a number of samples of commercial indigo:

| Description. | Specific gravity. | Ash. | Indigotin. |
|---|---|---|---|
| Kurpah blue | 1.129 | 17.54 | 55.11 |
| Watson's best | 1.292 | 6.50 | 59.53 |
| Bengal red | 1.391 | 6.41 | 54.03 |
| Oude | 1.427 | 7.02 | 52.90 |
| Bengal blue | 1.431 | 7.50 | 57.60 |
| Kurpah red | 1.529 | 21.20 | 45.28 |
| Guatemala | 1.559 | 14.49 | 47.04 |

Indigo preparations have been referred to under processes (see p. 455), and it was then noted that the salts of the indigo-sulphonic acids constituted the several so-called indigo extracts. *Indigo-carmine* is the potassium or sodium sulphindigotate ($C_{16}H_8(SO_3K)_2N_2O_2$). It comes into commerce in

* Amer. Journ. Anal. Chem., ii. p. 130.

both paste and solid form. It is soluble in one hundred and forty parts of cold water, readily soluble in dilute sulphuric acid. It dyes animal fibres direct, but with a much lighter shade than indigo, and is not at all so fast to light, while to vegetable fibres it shows no affinity. An analysis of the several grades of carmine-paste by Mierzinski * gave :

| DESCRIPTION. | Water. | Indigo. | Salt. |
|---|---|---|---|
| Carmine I. . . . . . . . . . . . . | 89.0 | 4.96 | 5.7 |
| Carmine II. . . . . . . . . . . . . | 85.0 | 10.02 | 4.8 |
| Carmine III. . . . . . . . . . . . | 73.7 | 12.04 | 13.9 |

*Saxony Blue* (*Chemic Blue*) is the free sulphindigotic acid, $C_{16}H_8N_2O_2(SO_3H)_2$, and forms a deep-blue solution. It is prepared as in the making of indigo-carmine, except the acid is not saturated with alkali. It was largely used in dyeing wool, but is not adapted for silk. *Indigo-purple* is a reddish-violet powder, which mixed with varying amounts of orseille can be used for dyeing wool directly without mordants. For its preparation, powdered indigo is covered with ordinary (not fuming) sulphuric acid, and having been cooled is left for half an hour. In this way is obtained a blue solution of sulphindigotic (indigo-disulphonic) acid, which can be worked up into indigo-carmine and a violet powder. This latter is the monosulphonic acid, which is washed first with water and then with dilute soda solution until the washings are no longer acid, then dried for use as above. A product of analogous composition, known as *Boiley's Blue*, is prepared by gradually adding one part of finely-powdered indigo to ten or twenty parts of acid sodium sulphate, $HNaSO_4$, in a state of fusion. The product is dissolved in water, precipitated with common salt, and washed with brine. Boiley's blue is a crystalline light-purplish mass, soluble in water with beautiful blue-violet color. Its solution in strong boiling acetic acid deposits on cooling large prismatic crystals exhibiting a coppery reflection. It is insoluble in alcohol or ether, but readily soluble in hot water. The light transmitted by the solution is red. With barium and strontium salts it yields violet precipitates.

The fact that indigo had been obtained artificially by several different methods was mentioned under the artificial dye-colors. (See p. 420.) A synthesis of indigo-carmine has also been effected within recent years. The process, due to B. Heymann,† is as follows : One part of phenyl-glycocoll ($C_6H_5.NHCH_2.COOH$) is rubbed up with ten to twenty times its volume of clean sand (which simply acts in the way of reducing the temperature of the reaction), and slowly added to fuming sulphuric acid, with eighty per cent. anhydride strength, warmed to 20° or 25° C. Care is to be taken that the temperature does not thereby exceed 30° C. After the solution of the phenyl-glycocoll, which takes place with evolution of sulphurous oxide, concentrated sulphuric acid of 66° B. is added to remove the excess of anhydride. It is then diluted with ice and common salt added, when indigo-carmine (indigo-disulphonic acid) at once separates out. Experiments on dyeing with the new product show it to be better and purer than the commercial indigo-carmine. Its identity was established in a number of ways.

* Ganswindt, Färberei, p. 150. † Ber. Chem. Ges., xxiv. p. 1476.

The yield at present amounts to sixty per cent. of the theoretical, but this may be improved by further study of the conditions of the reaction.

(*b*) *From Logwood.—Logwood Extracts* are prepared as liquids of 12°, 42°, and 51° Tw. (for equivalents of the Beaumé scale, see Appendix) and as a solid. This latter forms a dry black, lustrous and resin-like mass, which is quite brittle and easily powdered, tastes sweetish astringent, and yields a reddish-brown solution. The specific gravity ranges from 1.45 to 1.51. The specific gravity is not a reliable indication of the strength of the fluid extract, as it is liable to be raised by the addition of salt, glucose, molasses, etc. The extracts are also sometimes adulterated with starch, dextrin, chestnut-bark extract, hemlock extract, etc. The following table by Brühl * gives the yields of extracts obtained by himself from different woods and the percentage solubility of the resulting extracts in ether and alcohol. The portion dissolved by ether represents roughly the hæmatoxylin percentage, while that dissolved by absolute alcohol represents the hæmatëin and decomposition products of the hæmatoxylin.

| Description of Wood. | Yield of extract. | Soluble in ether. | Soluble in absolute alcohol. | Residue. |
|---|---|---|---|---|
| Yucatan | 20.20 | 60.12 | 87.46 | 2.42 |
| Yucatan, E. J. | 17.34 | 58.34 | 38.51 | 3.15 |
| Laguna | 21.00 | 51.37 | 47.95 | 0.68 |
| St. Domingo | 14.02 | 44.95 | 53.47 | 1.58 |
| St. Domingo, O. | 19.30 | 43.81 | 50.32 | 5.87 |
| Monte Christo, 1884 | 18.75 | 32.00 | 60.32 | 7.68 |
| Monte Christo, 1887 | 14.00 | 34.72 | 54.10 | 11.18 |
| Fort Liberté, 1886 | 20.33 | 41.89 | 54.11 | 4.00 |
| Fort Liberté, 1887 | 16.00 | 50.00 | 47.92 | 2.08 |
| Fort Liberté, 1885–86 | 17.45 | 59.72 | 35.17 | 5.21 |
| Fort Liberté, J. B., 1887 | 18.00 | 59.24 | 34.81 | 5.95 |
| Jamaica | 18.70 | 43.20 | 50.50 | 6.30 |
| Jamaica | 18.00 | 43.05 | 50.71 | 6.24 |
| Jamaica wood roots | 10.70 | 52.99 | 30 12 | 16.89 |

*Indigo Substitute* (*Noir imperial*, or *Kaiserschwarz*).—Under these names are known oxidized logwood extracts, made by boiling logwood extract with copper, iron, or chromium salts with the addition of oxalic acid. They may be in liquid form, or pastes, or dry powders. The preparations are almost insoluble in water, but completely soluble in acids with yellowish-brown color. A commercial preparation of this class, known as "direct black," for cotton forms a brownish, viscid liquid, composed of fifty per cent. water, forty-five per cent. of a substance soluble in alcohol and ether (hæmatoxylin and hæmatëin), and 3.5 per cent. of copper sulphate. *Hæmatëin* (*Hématin*) is a commercial preparation of French origin, which claims to consist of nearly pure dyestuff. It forms a granular, reddish-brown powder, completely soluble in water, and dyes the same shades as those obtained from the wood. Fifteen kilos. of hæmatëin are said to be equivalent to one hundred kilos. of the logwood.

(*c*) *Litmus*, as has been said, is a mixture of the lichen dye of that name with chalk or gypsum as inert material. It is made in different numbered grades, containing different amounts of the mineral matter. Lit-

* Textile Colorist, x. p. 148.

mus in the dry form has a violet-blue color, is quite friable, and dissolves in water and dilute alcohol, leaving a residue of chalk, gypsum, alumina, silica, etc.

4. FROM BROWN DYES.—(a) *Catechu* has been described already in part under the raw materials of the tanning industry. (See p. 322.) It is not unfrequently adulterated with starch, sand, clay, and blood. Good catechu should yield at least half its weight to ether and should be entirely soluble in boiling water, the latter solution depositing catechu on cooling. Catechu does not wholly dissolve in cold water unless it has been previously modified by age or exposure to damp. It should not yield more than five per cent. of ash. *Prepared Catechu* has been merely purified by mechanical means. For this purpose, the commercial catechu is fused on the water-bath, whereby sand, earth, and similar impurities settle out, and then it is strained to remove leaves, etc. The material so obtained is again melted on the water-bath, and to every one hundred parts of the catechu three-fourths per cent. of potassium bichromate is added, when it is allowed to cool down again.

## IV. Analytical Tests and Methods.

1. FOR DYE-WOODS.—Here the question of adulteration does not come notably in play. The compact woods are not capable of much adulteration of any kind. When chipped or rasped, however, they may be adulterated quite considerably. The examination with the microscope or simple lens will often suffice to indicate the nature of this adulteration. A special case of cheapening is that of the cured or fermented logwood chips, which, as has already been stated, may take up as the result of this fermentative process as much as thirty to forty per cent. of water. In this case a moisture determination will show the change, allowance being made for the fourteen per cent., which is the average moisture of the unfermented wood.

To determine the comparative dyeing value of different samples of woods, the only thoroughly reliable test is an actual dyeing test made with definite weights of the wood, thoroughly extracted, and using definite amounts of mordants upon the wool or other fibre used. This test, as applied to logwood, for example, would be carried out as follows: * "Some white wool is boiled in a solution of potassium bichromate containing such an amount of the salt as will correspond to three per cent. of the weight of the wool. The mordanted wool is then introduced in small successive portions into the hot liquid to be tested (logwood decoction or extract), when it will be dyed black, and the weight which can be thus dyed will be an indication of the amount of the coloring matter. This method of logwood assay takes cognizance both of the actual and the potential coloring matter present (hæmatëin and hæmatoxylin), and is a more rational method of examination than any based on the color produced on cotton mordanted with alumina or tin salts." The dye test in other cases must be made upon a normal prepared extract of known strength and purity, and the result compared with those obtained with a corresponding weight of the supposed adulterated sample.

2. FOR DYE-WOOD AND OTHER EXTRACTS.—(a) *Orseille Extract.*—This may be adulterated with logwood or Brazil-wood extract. They may be de... according to Leeshing, as follows: A solution of orseille extract, much

* Allen, Commercial Organic Analysis, 2d ed., iii. p. 380.

diluted and acidified with acetic acid, will, if pure, when boiled with a freshly prepared solution of stannous chloride, become pale yellow or almost colorless, while logwood extract solution under similar circumstances will show a violet color and Brazil-wood solution a red color. If, therefore, the orseille is adulterated with logwood extract a permanent grayish-blue color will show, if with Brazil-wood extract, a reddish color.

Orseille is also found frequently to have been adulterated with aniline dyes, especially magenta, acid magenta, and methyl violet. For the detection of magenta and methyl violet Knecht* employs cotton yarn dyed with chrysamin (p. 419). This does not take up the coloring matter of the orseille, but is dyed red by magenta and brownish-red by methyl violet. To detect the acid magenta, Kertesz † treats the orseille preparation with benzaldehyde and adds to the solution tin salt and hydrochloric acid, shaking up the mixture thoroughly. If acid magenta was present a red color will remain, while with pure orseille the solution remains colorless. One part of acid magenta in one thousand parts of orseille it is said can be thus detected. For other tests for the artificial dye-colors when present as adulterants in orseille, see Allen, "Commercial Organic Analysis," 2d ed., iii. pp. 322 and 323.

(b) *Quercitron Extracts.*—The dyeing value of the extract, as well as a possible adulteration of the same with dextrin, glue, etc., can be best determined by an actual dye test. For this purpose, wool is boiled with 1.5 per cent. of tin salt and three per cent. of oxalic acid, then washed. One gramme of the wool is now dyed with twenty cubic centimetres of a solution of ten grammes of the quercitron extract in one thousand cubic centimetres of water. Similarly several portions of one gramme each of mordanted wool are dyed with solutions of pure bark or pure extract of definite strength, and the results compared.

(c) *Annatto* (*Orlean*).—Annatto possesses only a slight importance as a dyeing agent, but special importance as the basis of most butter colorings. (See p. 270.) It is therefore a commercial article of common use and liable to be adulterated. The common adulterants are starch, dextrin, chalk, silica, alumina compounds, and common salt, together with ochre, brick-dust. Most of these increase notably the percentage of ash, which in a pure sample it is said should not exceed ten to twelve per cent. Wynter Blyth gives the following two analyses as illustrating the nature of its adulteration:

| Description. | Water. | Resin. | Extractive matter. | Ash. |
|---|---|---|---|---|
| Fair commercial sample . . | 24 2 | 28.8 | 24 5 | 22.5 |
| Adulterated sample . . . . | 13.4 | 11.0 | 27.3 | 48.3 } Oxide of iron, alumina, silica, chalk, and salt. |

For dyeing purposes the only satisfactory test is an actual dyeing test in comparison with an authentic unadulterated sample. For the analysis of the many butter-coloring mixtures containing annatto as the basis the reader is referred to Allen, "Commercial Organic Analysis," 2d ed., iii. pp. 353–356, and Wynter Blyth, "Foods, Composition and Analysis," p. 306.

* Journ. Soc. Dyers, etc., ii. p. 58.

† Dingler, Polyt. Journ., 256, p. 281.

(*d*) *Logwood Extract.*—Both the liquid and the solid extracts are liable to be adulterated, the former with glucose, molasses, dextrin, salt, and other extracts of lesser value, the latter with starch and inferior extracts. Notably are the French and German logwood extracts adulterated in the way just referred to. The following analyses of some of the commercial extracts as currently sold in France and Germany are given by V. H. Soxhlet:*

| Description of Extract. | Molasses. | Dextrin. | Chestnut extract. | Salt. |
|---|---|---|---|---|
| Guaranteed Pure, 30° B. . . | 5 per cent. | | | |
| Prima, 30° B. . . . . . . | 10 " " | | | |
| Secunda, 30° B. . . . . . . | 20 " " | . . . . . | 10 per cent. | 10 per cent. |
| Secunda, Solid . . . . . . | 20 " " | . . . . . | 15 " " | |
| Sanford Brand, I. . . . . . | 25 " " | 15 per cent. | | |
| Sanford Brand, II. . . . . | 35 " " | 10 " " | 10 " " | |
| Sanford Brand, III. . . . . | 35 " " | 15 " " | 15 " " | |

The Sanford Brand here referred to is a French extract made in imitation of the original American Sanford Extract.

The extracts may be tested for purity either by the colorimetric assay or by comparative dye tests. The colorimetric test is carried out, according to Henry Trimble,† as follows: A volume of solution corresponding to .001 gramme of the *dry* extract is treated with ten cubic centimetres of water naturally or artificially containing traces of calcium carbonate and a solution of .002 gramme of crystallized copper sulphate. The mixture is brought quickly to the boiling-point and diluted with distilled water to one hundred cubic centimetres. The color of this solution is then compared with one of pure hæmatoxylin similarly treated, or with a standard sample of logwood extract.

The method of carrying out the dye test for logwood with bichromate of potassium mordant has already been given in speaking of dye-woods. The same test is, of course, equally applicable to the extracts. Cotton strips are sometimes used for these dye tests instead of wool. The cotton strips must be boiled in dilute soda solution and well washed. They may then be mordanted with nitrate of iron solution instead of the chromium salt, following the nitrate of iron with a rinsing in carbonate of soda solution and thorough washing. They are then put in the dye-bath cold, and this gradually heated to boiling. In this dye-testing with iron solution, the hæmatoxylin of the solution is oxidized by the ferric oxide to hæmatëin, so that the full coloring value of the logwood is obtained in the test.

For the discovery of adulterations like chestnut extract, which contain almost nothing soluble in ether, Houzeau proceeds as follows: One gramme of the extract to be investigated is dried at 110° C., exhausted with ether, and the weight of the dissolved material determined. The undissolved material is then exhausted with absolute alcohol, and the weight of the portion dissolved by this also determined. The comparison of the figures so obtained with those yielded when a pure extract is treated with the same solvents will show clearly the presence or absence of adulterating extract. Dye tests may also be carried out with the material which has

* Färber-Zeitung, Aug. 1, 1890, p. 368. † Journ. Soc. Dyers, etc., i. p. 92.

been extracted by ether and alcohol respectively in the two cases, and the difference more fully established.

(*e*) *Catechu Extract.*—Catechu is frequently adulterated, not only with mineral matter like sand and clay, but with starch, dextrin, sugar, blood, etc. The mineral matters will, of course, remain in the ash. This in normal catechu should not exceed five per cent. The starch may be detected by extracting the sample with alcohol, boiling the insoluble residue with water, and testing the cooled liquid with iodine, which will show by the blue color any starch present. An addition of alcohol to the aqueous solution will show by the production of a turbidity any notable quantity of dextrin. Blood may be detected by treating the sample with alcohol, and drying and heating the residue in a tube, when ammonia and offensive decomposition products will be given off, or the coagulation of the blood albumen when the aqueous solution is boiled.

The value of catechu for dyeing purposes can only be determined by a dye test. For this purpose strips of cotton-stuff are immersed for half an hour in a catechu solution (for each gramme of the cotton fifty cubic centimetres of a catechu solution containing five grammes to the litre of water are taken and diluted with water if necessary). The strips are pressed out, and then the color developed by oxidizing in a hot solution of one to two grammes of potassium bichromate to the litre of water.

3. For Cochineal.—The adulteration of cochineal may be effected in various ways. A very common adulteration is to admix with the fresh cochineal insects others from which the coloring power has already been in large part extracted. To give the exhausted cochineal insects the appearance of fresh ones, they are shaken up with talc, barytes, and white lead, and thus given a coating resembling the silvery insects. Either a washing or an ash determination will serve to detect this adulteration. The valuation of the cochineal as to coloring power may be made by several methods. The one best known is that of Penny,* in which one gramme of the cochineal is treated with fifty grammes of dilute potassium hydrate, twenty-five grammes of water added, and to this is then added drop by drop a solution of ferricyanide of potassium containing five grammes to the litre. The solution loses its purplish-red color and becomes brownish-yellow. The action of the ferricyanide of potassium solution is tested in comparison on the solution of one gramme of a cochineal of known purity. Liebermann † extracts the cochineal with boiling water, and determines the coloring matter by the addition of a slightly acid solution of lead acetate. After filtering and washing the lead precipitate, a lead determination is made in an aliquot portion, and from this the percentage of coloring matter calculated. Allen does not consider either of these methods to be perfectly satisfactory. An actual dye test is therefore in the end to be regarded as the most reliable method of valuation. For this purpose strips of woollen stuff of about five grammes in weight are put into the bath until the color is all taken up. A portion of the strips may then be dyed scarlet-red by immersing them in a tin solution (for one gramme of cochineal two grammes of cream of tartar, two grammes of tin salt, and as much water as is needed to thoroughly immerse the strips), and the other portion of the strips may be dyed a cherry-red by the use of an alum solution (for one gramme of cochineal, three-fourths gramme of cream of tartar and one and a half

* Journ. für Prakt. Chem., 71, p. 119. † Berichte der Chem. Ges., xviii. p. 1970.

grammes of alum). These strips are then to be compared with others obtained from similar treatment of a normal or pure cochineal sample.

4. FOR INDIGO AND ITS PREPARATIONS.—Indigo may be of very varying value as it comes into commerce, partly because of the differences natural to such a product and dependent upon the differences in cultivation of the plant, care in extracting and drying the indigo, and the fact that the natural product is at best a mixture, and partly from intentional adulteration. Thus starch colored with iodine, Prussian blue, smalt, and logwood-powder are said to be used as adulterants of commercial indigo. In order to detect the starch, the suspected sample is rubbed up in a mortar with chlorine-water until it is completely decolorized, when a drop of potassium iodide is added. If starch be present the blue color of iodide of starch will be seen. To detect the smalt or Prussian blue, the sample is oxidized with nitric acid, when if a blue residue is shown in the yellowish solution adulteration is indicated. If the adulterant were Prussian blue, the color fades too after a time, if smalt, it is permanent. To detect logwood-powder, mix the sample with oxalic acid, place it upon filter-paper, and moisten it; in the presence of logwood the paper will be colored red, if the sample were pure it is unchanged.

In the assay of commercial indigo the *moisture* is generally to be determined. This should not exceed some seven per cent. in a genuine sample. The *ash* similarly is an important criterion of the quality of the indigo sample. In the purest kinds it is sometimes as low as two per cent., but from five to eight per cent. is more usual. Some of the inferior grades of indigo, such as Kurpah and Madras, may contain from twenty-five to thirty-five per cent. of ash.

The methods for the determination of the percentage of indigo-blue are, of course, the most important things to be considered in connection with indigo as a dyeing material. They are very numerous. We may summarize the more important of them under three heads,—viz., oxidation methods, reduction methods, and sublimation of the pure indigo-blue from the commercial product.

The oxidation of the indigo-blue takes place in acid solution, the indigo being previously dissolved in strong sulphuric acid. Potassium permanganate, bichromate, and ferricyanide have all been recommended and used in this connection. All the processes are open to the objection that the oxidizing agents act on the indigo-gluten and ferrous salts as well as on the indigo-blue and indigo-red, but the errors due to this cause may be practically avoided, as pointed out by Rawson, by previously precipitating the sulphindigotic acid in the form of the sodium salt by adding common salt to the solution. The method with permanganate of potassium, modified in this manner by the use of common salt, is as follows:* One gramme of the sample of indigo in the form of an impalpable powder is mixed in a small mortar with its own weight of ground glass. This mixture is gradually added with constant stirring to twenty cubic centimetres of concentrated sulphuric acid (specific gravity 1.845), which is then heated to about 85° C. for an hour. The product is then cooled, diluted with water to one litre, and filtered from indigo-brown and other soluble matter. Fifty cubic centimetres of the filtered solution are now taken diluted with fifty cubic centimetres of water, and thirty-two grammes of common salt added, which

* Allen, Commercial Organic Analysis, 2d ed., iii. p. 308.

quantity is almost sufficient to saturate the liquid. After standing for two hours, the solution is filtered, and the precipitate washed with about fifty cubic centimetres of brine of 1.2 specific gravity. This sodium sulphindigotate is dissolved in hot water, the solution cooled, mixed with one cubic centimetre of sulphuric acid, and diluted to three hundred cubic centimetres. This solution is then titrated in a porcelain dish with a solution of potassium permanganate containing .5 gramme of the solid salt per litre, the exact oxidizing power of which has been ascertained by experiment with a solution of pure indigotin. The oxidation is regarded as complete when the liquid which at first takes a greenish tinge changes to a light yellow with a faint pink color on the margin.

The reduction of indigo-blue may take place in alkaline solution or with a solution of the sulphindigotic acid or its salts. Ferrous hydroxide and hyposulphites are among the reducing agents used to effect the reduction in alkaline solutions. C. Rawson considers the hyposulphite reduction method the better one of the two. In carrying it out, one gramme of the finely-powdered sample is made into a paste with water and placed in a flask with about six hundred cubic centimetres of lime-water. The flask is closed by a cork having four perforations, two of which serve for the passage of coal-gas, a third carries a siphon, while to the fourth is fitted a tap-funnel. The contents of the flask are heated to 80° C. and one hundred to one hundred and fifty cubic centimetres of a strong solution of sodium hyposulphite ($NaHSO_2$) introduced through the tap-funnel. In a few minutes the liquid assumes a yellow tint, and is maintained at a temperature near the boiling-point for half an hour. After allowing the insoluble matters to subside, an aliquot portion of the solution should be removed, and a current of air drawn through it for about twenty minutes, when it is acidulated with hydrochloric acid. The precipitate, which consists of indigotin and indigo-red, is collected on a weighed filter, washed with hot water, dried at 100° C., and weighed. It is then exhausted with boiling alcohol, whereby the indigo-red is dissolved out and the difference again weighed as indigo-blue. Rau reduces the indigo in alkaline solution with glucose, and L. M. Norton uses milk of lime and zinc-dust as reducing agent, and then takes an aliquot portion of the reduced solution to reduce a solution of iron-alum. The ferrous salt formed corresponds to the reduced indigo in the volume taken, and is determined by titration with a standard solution of potassium bichromate. (For details, see Helen Cooley's article, Amer. Journ. Anal. Chem., ii. p. 133.)

For the reduction of the indigo in acid solution, Bernthsen and Drew * recommend the use of hyposulphite of soda ($NaHSO_2$), and claim that the reaction is a quantitative one: $C_{16}H_8N_2O_2(SO_3H)_2 + NaHSO_2 + H_2O = C_{16}H_{10}N_2O_2(SO_3H)_2 + NaHSO_3$.

C. Rawson † considers that of all the volumetric methods which have been devised for estimating indigotin the hyposulphite process is capable of giving the most rapid and accurate results, but that considerable care and delicacy are required in its manipulation.

Lee ‡ has proposed the sublimation of the indigo-blue as a method for determining its percentage in commercial indigo. Other writers, however, do not agree that, unless the indigo has previously been somewhat purified, the results can be depended upon.

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* Chem. News, xliii. p. 80. † Allen's Com. Org. Anal., 2d ed., iii. p. 309.
‡ Chem. News, l. p. 49.

## REACTIONS OF THE MOST IMPORTANT NATURAL DYESTUFFS.

| Dyestuffs. | Aqueous extract. | Caustic soda, 1 : 10. | Aluminum sulphate and sodium carbonate, 1 : 10. | Ferric chloride, 1 : 10. | Calcium chloride, 1 : 10. | Hydrochloric acid, 1 : 10. | Remarks. |
|---|---|---|---|---|---|---|---|
| Madder | Dirty red. | Bluish red. | Red. | Dark brown precipitate. | Red precipitate. | Red precipitate. | . . . . . . . . |
| Sandal-wood | No extraction. | Bluish-red extract. | Red. | Brown-black precipitate. | Red precipitate. | Red precipitate. | With alcohol, reddish extract. |
| Logwood | Bluish red. | Violet precipitate. | Reddish-violet solution. | Black solution. | Red precipitate in concentrated solution. | Yellowish-red color. | . . . . . . . . |
| Old Fustic | Reddish yellow. | Violet precipitate. | Yellow solution. | Black precipitate. | Red precipitate in concentrated solution. | Yellow-red color. | . . . . . . . . |
| Young Fustic | Red solution. | Bluish-red color. | Reddish-yellow solution. | Dark olive precipitate. | Red precipitate. | Bright yellow color. | . . . . . . . . |
| Quercitron | Reddish yellow. | Red color. | Yellow precipitate. | Dark green precipitate. | Yellow precipitate. | Bright yellow color. | Flavine. |
| Turmeric | Yellow solution. | Red color. | Yellow precipitate. | Yellow precipitate. | Yellow precipitate. | Bright yellow color. | . . . . . . . . |
| Annatto | Yellow solution. | Yellow color. | Yellow solution when poured over. | Black precipitate, turning blue with sulphuric acid. | Red precipitate. | Red color. | Dyes cotton in alkaline solution. |
| Catechu | Turbid yellowish-brown solution. | Clear reddish-yellow color. | Yellow color. | Dark green precipitate. | Yellow precipitate. | Bright yellow precipitate. | With potassium bichromate, red-brown on heating. |
| Prepared Catechu | Clear yellowish-brown solution. | Reddish-brown precipitate. | Yellow color. | Bright olive color. | Yellow precipitate. | Bright yellow precipitate. | With potassium bichromate, yellow-brown. |
| Gallnuts | Dirty yellow color. | Reddish-yellow precipitate. | Light yellow color. | Blue-black precipitate. | Turbidity. | Bright yellow precipitate. | . . . . . . . . |
| Sumach | Dirty yellow color. | Reddish-yellow precipitate. | Yellow color. | Black precipitate. | Yellow precipitate. | Bright yellow precipitate. | . . . . . . . . |
| Cochineal | Bluish-red color. | Bluish-red solution. | Red color. | Black color. | Black precipitate. | Yellow-red color. | . . . . . . . |
| Tannin | Colorless. | Light yellow precipitate. | Light yellow precipitate. | Blue-black precipitate. | Turbidity. | Bright yellow precipitate. | . . . . . . . . |
| Lac Dye | Red color. | Bluish-red solution. | Red color. | Gray precipitate. | Red precipitate in concentrated solution. | Yellow color. | . . . . . . . . |
| Cudbear | Bluish-red color. | Bluish-red solution. | Bright red color with aluminum sulphate. | Bright red color. | Red precipitate in concentrated solution. | Yellow-red color. | Orseille. |

C. Rawson * has given the following results with commercial samples, using the several processes just detailed:

| METHOD USED. | Java. | Bengal. | Bengal. | Oude. | Kurpah. | Madras. |
|---|---|---|---|---|---|---|
| Water | 2.99 | 5.22 | 6.17 | 7.50 | 8.05 | 5.71 |
| Ash | 1.99 | 3.91 | 4.86 | 8.21 | 25.72 | 33.62 |
| Indigotin, by sublimation | 60.84 | 57.50 | 49.36 | 41.60 | 41.92 | 39.56 |
| Indigotin, volumetric, by hyposulphite | 68.78 | 59.26 | 55.66 | 43.18 | 42.52 | 36.80 |
| Indigotin, gravimetric, by ferrous sulphate and NaOH | 68.24 | 58.84 | 54.34 | 44.50 | 41.50 | 34.50 |
| Indigotin, gravimetric, by hyposulphite and lime | 68.97 | 59.12 | 56.20 | 43.42 | 42.68 | 35.21 |
| Indirubin, separated by alcohol | 4.23 | 3.50 | 2.80 | 3.65 | 2.45 | 3.98 |
| Indigotin and indirubin, titration with $KMnO_4$ direct | 76.18 | 66.71 | 62.66 | 50.04 | 47.15 | 39.50 |
| Indigotin and indirubin titration after precipitation with salt | 73.55 | 63.50 | 57.50 | 44.90 | 43.10 | 37.40 |

The table from Dammer's Chem. Technologie, Band iv. p. 591 (see opposite page), shows the characteristic reactions of the important natural dyestuffs.

## V. Bibliography and Statistics.

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### STATISTICS.

1. INDIGO PRODUCTION AND EXPORTS.—The annual production of natural indigo in 1890 was estimated to be as follows:

| | | |
|---|---|---|
| Bengal | 4,000,000 kilos., valued at | $10,000,000 |
| Madras | 1,100,000 " " " | 2,000,000 |
| Manila, Java, Bombay | 1,000,000 " " " | 2,500,000 |
| Central America | 1,125,000 " " " | 3,000,000 |
| China and other countries | 1,000,000 " " " | 2,500,000 |
| | 8,225,000 | $20,000,000 |

* Allen, Commercial Organic Analysis, 2d ed., iii. p. 311.

In more recent years the cultivation of indigo has diminished. The East Indian production for the last five years has been as follows:

| | |
|---|---|
| 1895 . . . . . . . . . . . . . . | 162,000 maunds (1 maund = 37.3 kilos.). |
| 1896 . . . . . . . . . . . . . . | 158,923 " |
| 1897 . . . . . . . . . . . . . . | 110,000 " |
| 1898 . . . . . . . . . . . . . . | 124,500 " |
| 1899 . . . . . . . . . . . . . . | 85,000 " |

According to Dr. George Watt's report to the Indian government there were in India 2762 indigo factories and 6032 vats, giving employment to 356,675 persons during the working season, a calculation that does not include the agricultural labor necessary to produce the plant. (Journ. Soc. Chem. Ind., 1894, p. 994.)

The exportations of indigo from India in recent years have been as follows:

| | 1887-88. Chests. | 1888-89. Chests. | 1894-95. Chests. | 1897-98. Chests. |
|---|---|---|---|---|
| Germany, Austria, and Holland . . | 9,900 | 10,836 | 11,463 | 8.740 |
| England . . . . . . . . . . . . . . | 6,300 | 6,085 | 8,931 | 6.590 |
| France, Switzerland, and Italy . . . | 6,000 | 8,965 | 5,972 | 4.160 |
| Russia . . . . . . . . . . . . . . . | 2,600 | 2,815 | 1,815 | 1.660 |
| America . . . . . . . . . . . . . . | 7,500 | 9,263 | 8,917 | 6.940 |
| Arabia and the Levant . . . . . . | 700 | 648 | 2.876 | 3.080 |
| Total . . . . . . . . . . . . | 33,000 | 83,612 | 39,974 | 31.170 |

2. Exportations of Dye-woods.—The exportations of several of the more important dye-woods from tropical American countries for the period given have been as follows:

1. *Logwood Exports:*

| | From Haiti. Pounds. | From Haiti. Value. | From Jamaica. Pounds. | From Jamaica. Value. |
|---|---|---|---|---|
| 1882-83 . . . . . | 152,288,713 | $1,998,789 | 66,685,584 | $434.632 |
| 1883-84 . . . . . | 154,775,887 | 2,031,434 | 100,638,496 | 655.921 |
| 1884-85 . . . . . | 142,986,254 | 1,876,695 | 126,795,200 | 743.774 |
| 1885-86 . . . . . | 114,341,436 | 1,500,731 | 142,256,128 | 927.165 |
| 1886-87 . . . . . | 105,000,065 | 1,378,125 | 132,009,472 | 932.089 |
| 1887-88 . . . . . | 106,163,734 | 1,893,399 | 226,108,912 | 1,718.627 |
| 1888-89 . . . . . | 57,021,431 | 748,406 | 258,616,960 | 1,826.035 |
| 1889-90 . . . . . | 70,801,241 | 929,266 | 133,232,400 | 962.432 |
| 1890-91 . . . . . | 56,743,891 | 744,764 | 244,794,592 | 1.861.395 |
| 1891-92 . . . . . | 39,766,320 | 521,933 | 194,152,784 | 1,476.320 |
| 1892-93 . . . . . | . . . . | . . . . | 207,472,832 | 1,633.947 |

2. *Fustic Exports:*

| | From Mexico. Pounds. | From Mexico. Value. | From Jamaica. Pounds. | From Jamaica. Value. |
|---|---|---|---|---|
| 1882-83 . . . . | 30,746,240 | $280,988 | 7,477,792 | $48,738 |
| 1883-84 . . . . . | 32,995,200 | 248,656 | 4,024,272 | 21,857 |
| 1884-85 . . . . . | 17,471,509 | 128,019 | 2,078,160 | 13,093 |
| 1885-86 . . . . . | 17,420,099 | 110,873 | 8,526,768 | 21,071 |
| 1886-87 . . . . . | 24,942,407 | 178,621 | 9,366,000 | 61,044 |
| 1887-88 . . . . . | 26,583,858 | 177,488 | 5.518,016 | 85,964 |
| 1888-89 . . . . . | 18,224,030 | 133,952 | 2,777,216 | 10,425 |
| 1889-90 . . . . . | 23,762,671 | 198,646 | 1,457,200 | 8,606 |
| 1890-91 . . . . . | 16,927,020 | 119,631 | 2,128,112 | 12,714 |
| 1891-92 . . . . . | 13,187,368 | 96,588 | 1,517,152 | 9,888 |
| [illegible]-93 . . . . . | . . . . . | . . . | 14,472,976 | 102,190 |

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3. *Exports of Brazil-wood from Bahia during Ten Years Past:*

| | To United States. Kilos. | To England. Kilos. | To Germany. Kilos. | To France. Kilos. | All other countries. Kilos. | Total Kilos. |
|---|---|---|---|---|---|---|
| 1884 | 584,318 | 143,480 | 15,000 | 336,189 | 56,350 | 1,135,337 |
| 1885 | 232,912 | 292,212 | 49,568 | 703,497 | . . . | 1,278,189 |
| 1886 | 684,002 | 193,189 | 134,857 | 904,348 | 18,569 | 1,934,965 |
| 1887 | 783,616 | 152,453 | 46,640 | 1,374,543 | . . . | 2,357,252 |
| 1888 | 388,631 | 84,341 | 18,584 | 369,725 | . . . | 861,280 |
| 1889 | 149,063 | 82,156 | 753,457 | . | . . . | 984,676 |
| 1890 | 58,121 | 166,198 | 78,959 | 127,016 | . . . | 430,295 |
| 1891 | 251,873 | . . . | . . . | 670,857 | 21,321 | 944,051 |
| 1892 | 635,030 | 64,676 | 25,782 | 1,093,650 | . . . | 1,819,138 |
| 1893 | 615,158 | 517,937 | 147,177 | 548,734 | 8,970 | 1,837,976 |

3. Importations of Dye-woods, Dye-wood Extracts, etc.—The United States importations of dye-woods and natural dyes for recent years have been:

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| Cochineal, lbs. | 161,330 | 142,261 | 158,055 | 97,563 |
| Valued at | $50,988 | $41,943 | $45,762 | $23,207 |
| Logwood, tons | 65,756 | 33,362 | 46,596 | 37,375 |
| Valued at | $1,516,855 | $611,010 | $741,455 | $546,274 |
| Cutch (catechu), Gambier, lbs. | 32,338,264 | 31,349,545 | 42,334,590 | 38,123,478 |
| Valued at | $1,158,611 | $959,501 | $1,021,341 | $754,497 |
| Indigo, lbs. | 3,340,001 | 3,522,016 | 3,097,340 | 3,127,357 |
| Valued at | $1,673,170 | $1,696,641 | $1,815,411 | $1,698,583 |
| Logwood and other extracts, lbs. | 4,839,111 | 5,562,264 | 4,084,672 | 3,183,864 |
| Valued at | $282,689 | $284,868 | $256,176 | $219,192 |
| Sumach (ground), lbs. | 13,432,041 | 18,688,635 | 8,301,235 | 12,975,970 |
| Valued at | $232,570 | $248,048 | $120,205 | $183,136 |

The English importations of dye-woods and natural dye-colors for the last four years have been:

| | 1896. | 1897. | 1898. | 1899. |
|---|---|---|---|---|
| Cochineal, cwt. | 5,697 | 4,729 | 4,961 | 3,823 |
| Valued at | £36,658 | £29,103 | £29,407 | £20,584 |
| Cutch and gambier, tons | 26,844 | 25,048 | 19,504 | 21,526 |
| Valued at | £548,756 | £418,128 | £304,998 | £347,025 |
| Indigo, cwt. | 89,941 | 82,526 | 53,838 | 58,977 |
| Valued at | £1,533,722 | £1,470,574 | £890,803 | £986,090 |

The German importations of dye-woods, etc., for the last four years have been:

| | 1896. Met. cent. | 1897. Met. cent. | 1898. Met. cent. | 1899. Met. cent. |
|---|---|---|---|---|
| Madder | 920 | 1,074 | 1,172 | 623 |
| Quercitron | 7,275 | 12,242 | 11,218 | 8,489 |
| Logwood | 444,737 | 367,795 | 283,389 | 287,347 |
| Fustic | 31,933 | 28,302 | 45,187 | 34,309 |
| Brazil-wood, etc. | 34,186 | 23,570 | 18,279 | 13,016 |
| Cochineal | 682 | 761 | 884 | 906 |
| Catechu and gambier | 90,115 | 57,912 | 64,872 | 72,371 |
| Indigo | 19,733 | 14,084 | 10,362 | 11,078 |
| Orseille and perseo | 1,133 | 1,716 | 1,678 | 840 |
| Sumach | 70,448 | 66,875 | 62,915 | 57,739 |
| Dye-wood extracts | 49,458 | 44,009 | 41,601 | 35,366 |

# CHAPTER XIV.

## BLEACHING, DYEING, AND TEXTILE PRINTING.

PRELIMINARY.—Prior to the operation of bleaching, except in cases where delicate shades are required, it is always necessary to thoroughly cleanse the fibre or fabric of grease and dirt. For *cotton*, which is generally handled as hanks, warps, and pieces, it is sufficient to boil it in a dilute solution of caustic soda or soda ash, followed by a good rinsing; it may, in some instances, be boiled in plain water, wrung out, and bleached or dyed; ordinarily, however, a boiling for two to three hours in a bath of eight to ten per cent. of crystallized soda and one to two per cent. of soap, calculated to the weight of the cotton, yields good result. The time for boiling out cotton is much reduced if it is immersed in a weak lukewarm bath of two per cent. sulphated oil strongly neutralized with ammonia or in a soap-bath containing ammonia. This is found to completely remove all natural oil on the fibres and thoroughly wet them. *Wool* is always thoroughly scoured both before and after it is manufactured into yarn. The soap solution generally employed contains from four to five ounces to the gallon of water, accompanied usually with a carbonated alkali (potash or ammonia) in about the following proportion: ten per cent. of soda and two per cent. of soap. The temperature of the bath being about 40° to 50° C. (See p. 307.) For *silk* (see p. 312) the scouring-bath contains about twenty-five to thirty pounds of Castile, Marseilles, or other *neutral soap* for each hundred pounds of silk, and a temperature at or near the boiling-point is taken for about two hours, turning the silk occasionally. For some colors a second scouring can be employed to advantage, only one-half the quantity of soap being used as in the first bath. It is the practice to use the baths several times, care being taken to enrich them with fresh soap.

*A.* BLEACHING.—This highly-important operation results in a more or less complete destruction of the natural coloring matter which is found in all fibres of industrial importance. Owing to the somewhat powerful action of most of the agents employed for the purpose, it will appear that, unless care and discretion are applied to their use on the part of the bleacher, something more than a destruction of the coloring matter will occur,—a probable partial destruction of the fibre. The operation has been known since the earliest times; the white linens of the Egyptians and Phœnicians were much esteemed by the nations trading with them. In the early part of the eighteenth century immense fields were given up wholly to bleaching in the United Kingdom; the process as carried out required several months, consisting of a successive treatment of the cloth or fabric in alkaline solution—termed "*bucking*"—and washing, then exposing, while damp, and spread out on the grass to the sunlight for a few weeks (*crofting*), immersing in sour milk, washing again, and finally exposing on the grass, these several operations being repeated until the required degree of whiteness is obtained. Great improvements in the above

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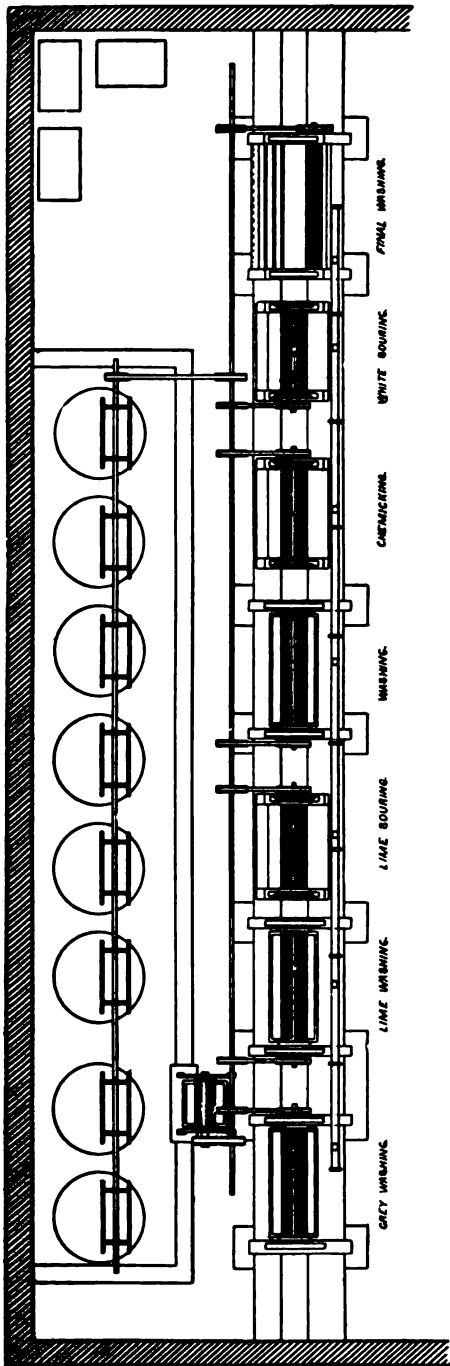
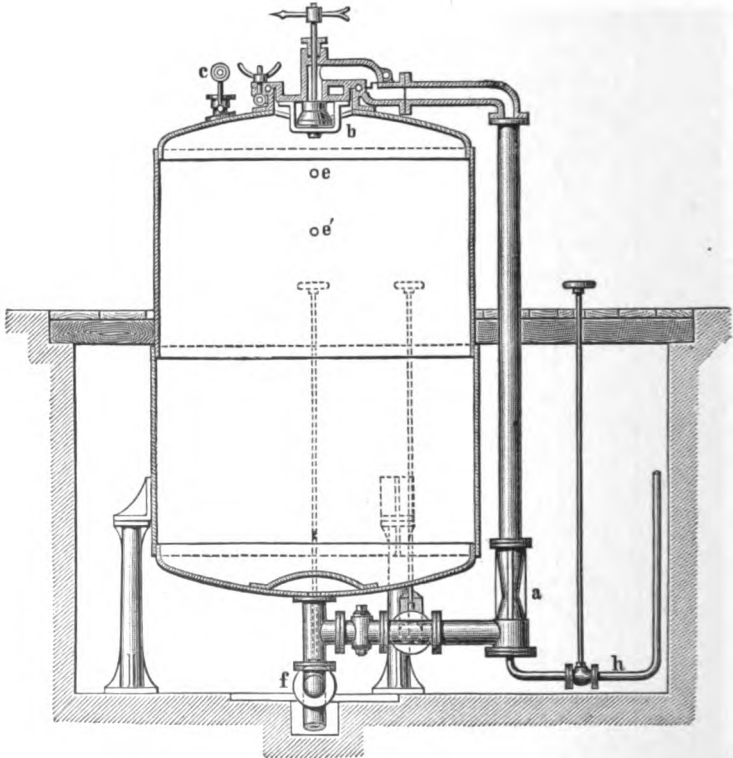
Fig. 122.

tedious process resulted when the use of sulphuric acid was substituted for the sour milk, and chlorine gas replaced the lengthy field exposure, this latter being due to M. Berthollet; but the general use of this substance was not established until the manufacture of the now familiar "chloride of lime" or "bleach." Since then many other bleaching agents, notably, hydrogen peroxide, have appeared, but whether they will ever displace the above is an uncertainty.

1. *Cotton* in the *raw* or *unmanufactured* state is rarely, if ever, bleached; as *yarn*, however, it is continually. The hanks, which have been previously scoured, are boiled in a solution of chloride of lime (*chemick*) from one to two hours, washed well in water, and passed through dilute sulphuric acid (1° Tw.) for about half an hour, and finally well washed. These operations can be easily conducted in the ordinary wooden tubs of the dye-house in places where much yarn does not have to be bleached, otherwise special arrangements should be provided. *Cotton warps* are similarly treated, the apparatus employed being a continuous (warp) dyeing-machine. *Cotton fabrics* require much care and skill, especially those intended for domestic use in the bleached condition, and also those which are to be afterwards dyed or printed with delicate shades. The method of bleaching, which has reached a high state of perfection, is the so-called "madder-bleach," from the fact that it is employed on all piece goods to be printed with alizarin. The process detailed and illustrated below must not be accepted as the exact method followed in every establishment,—it being remembered that nearly every bleacher has his own modifications which he introduces, but all yield the same result. The opera-

tion of stamping or sewing on designating marks; sewing the pieces together and singeing,—a removal of the nap or down from the cloth by means of a gas flame or curved hot plate ("singeing-plate"),—need not be detailed here; reference may be had to special works on textile manufacture.

Fig. 122 is a plan of part of a bleach-house for cotton cloth. The goods being received, they are passed through the first washing-machine, on the left of the figure; this operation has for its object the removal of loose dirt, grease,—added to the fabric during weaving,—and other matters; usually the goods are stacked overnight in order to allow an incipient fermentation to take place, when they are passed several times through the *lime-wash* (milk of lime) in order to become thoroughly impregnated with about five per cent. of lime, this being accomplished by means of rollers immersed in and below the surface of the lime-bath and a pair of squeezing or "nipping rollers."

Following the liming operation is the boiling ("bowking") in kiers; these are strong, wrought-iron cylindrical vessels, provided with a series of pipes, and in some cases with injectors, which enable the liquids contained in them to circulate completely through the cloth, which is previously introduced in the form of a rope. Fig. 123 is a vertical section of a single

Fig. 123.

injector-kier, and one well adapted for working at low pressures. Reference being had to the figure, the vessel being filled with the fabric, which is well laid in, the liquid is admitted, gradually finding its way to the false bottom,

through which it passes to the injector at *a*, where it meets a steam current, which forces it upward through the large pipe, finally being admitted to the kier again through the valve *b*, repeatedly following the circuit.

*Barlow's* high-pressure kiers are usually worked in pairs, and the liquid is forced from one to the other by the aid of steam. This kier has a central perforated tube, through which the liquid passes to come in contact with the cloth. Several other forms of kiers are in use, even open kettles acting as such, the object being the same in each case.

The length of time the cloth remains in the kier varies considerably, in some establishments, where a high-pressure is used (forty to fifty pounds per square inch), less time is required,—five to six hours being deemed sufficient; again, where a low-pressure is used (eight to twelve pounds) the goods are allowed to remain in from ten to twelve hours. From this boiling the pieces are *washed* in water, and passed through dilute hydrochloric acid (specific gravity 1.01 = 2° Tw.),—the bath being technically termed a "sour." The pieces are slowly worked until the lime is completely dissolved, when the goods are thoroughly washed, or until every trace of acid is removed, when a boiling with soap and soda follows in kiers exactly as in the boiling previously mentioned. For each hundred pounds of cloth a resin soap is used, made with five to six pounds of soda ash and one to two pounds of resin; the soda is dissolved in two gallons of water, the resin added, and the whole boiled for several hours; for each pound of cloth to be acted upon one gallon of water is used. The time required for this boil is nearly the same as in the previous boiling. When the resin soap solution is run off, the goods are boiled for three or four hours with a one per cent. solution of soda, to remove the soap and any unconverted resin remaining, followed immediately by a wash. At this stage of the process occurs the real whitening, or bleaching, of the goods,—the so-called "*chemicking*,"—requiring much care, and is performed with a solution made by dissolving chloride of lime, allowing to settle and become clear, the supernatant liquor alone being used. The strength of the solution, varying from ¼° Tw. to 2° Tw. (specific gravity 1.001 to 1.01), being used cold, or but slightly warmed, in the latter case penetrating the cloth better. Repeated passage of the goods through a weak solution is preferable to a shorter time in a strong solution, the danger from injury to the pieces being less. The next operation may be (not always) a wash, and then a *souring* in dilute (specific gravity 1.01) sulphuric acid,—termed a *white sour*,—after which the goods are allowed to remain for some time in a heap, but not long enough to become dry, as a tendering of the cloth will result; this is followed with a final wash to remove every trace of acid, passed through squeezing rollers, and over revolving cans heated by steam, to dry. The length of time required in the above process varies; if the goods are to receive a fine clear bleach, or are to receive delicate shades in dyeing and printing, four or five days may be necessary, but in the event of the goods being intended for full shades, half that time will answer.

*Mather-Thompson's Process.*—This is one of the newer processes, and is admirably suited for warps and piece-goods. The goods are sewed together, or tied, in the case of warps, subjected to the action of hot caustic alkali, washed, and transferred to wagons, the sides of which are of iron lattice-work (cages), and pushed into a horizontal kier, and for five hours acted upon by a solution of caustic soda (2° to 4° Tw. = specific gravity 1.01 to 1.02) delivered in a spray and at a pressure of four to five pounds. With-

out removing the goods from the kier they are washed with hot water, removed, and rinsed with cold water, completing the scouring. The bleaching is carried out in a continuous apparatus through the following stages:

1. Rinsing with warm water.
2. First chemick bath (chloride of lime solution, 1° Tw. = specific gravity 1.005).
3. Passage through atmosphere of carbonic acid gas.
4. Washing with cold water.
5. Worked through a one per cent. soda solution at 175° F.
6. Second washing.
7. Second chemick (chloride of lime solution .5° Tw.).
8. Second passage through carbonic acid gas.
9. Third wash.
10. Through one per cent. hydrochloric acid, or through one per cent. of a mixture of hydrochloric and sulphuric acid (2 : 1).
11. Final wash.

In this process the real bleaching is effected by the hypochlorous acid liberated by the action of the carbonic acid gas upon the calcium hypochlorite.

*Lunge's Bleaching Process* differs but slightly from others using chloride of lime, except that he increases the bleaching action by the use of a small quantity of some organic acid,—preferably acetic. Chloride of lime in contact with acetic acid forms calcium acetate, with evolution of free hypochlorous acid; this gives up oxygen during the bleaching, leaving hydrochloric acid, which acts on the calcium acetate, forming calcium chloride and regenerating the acetic acid. The hydrochloric acid never being in the free state cannot act on the fibre; acetic acid has no action, even at the high temperature or pressure used in bleaching.

*Hermite Process for Electrolytic Bleaching.*—This process is probably one of the most successful yet brought forward, embodying the use of electricity, effecting the bleaching by the decomposition of a four to five per cent. solution of *chloride of calcium* (not "chloride of lime," or "bleaching-powder"), of *magnesium*, or of *aluminum*. The electrolyzed solution of the salt employed is of especial service in causing the destruction of the coloring matter of vegetable textile fibres, but, owing to the peculiar effect of chlorine ... r silk, it is impracticable with them. Electrolyzed salt solutions ... ished by the addition of a quantity of salt equal to that absorbed ... res or fabrics when withdrawn from the bleach-bath.

... *en.*—This fibre is much more subject to the destructive action of ... agents than cotton, in consequence of which the same process is ... able, and also on account of the greater amount of impurities ... iefly pectic acid. For *yarns* the trade distinguishes three im... ades of bleaching,—*half*, *three-quarters*, and *full white*, to obtain ... rations are necessary:

... ree or four hours in a ten per cent. solution of soda ... ent. solution of caustic soda. Wash, rinse, and pass ... lers.

... a .4° Bé. solution of chloride of lime, and work or ... wash.

... o dilute sulphuric acid for one hour (one part acid to two ... water).

4. Boil again in a kier with two per cent. caustic soda.
5. Repeat the passage through chloride of lime and wash.
6. Final treatment with sulphuric acid as in No. 3.

The above will produce a *half-bleach*, and by repeating the three final operations a *full white* will be obtained. *Reeling* is a term particularly applicable to linen-bleaching, owing to the way the yarn is handled, the result being that the carbonic acid in the air acts upon and decomposes the chloride of lime, setting free hypochlorous acid, similarly to the use of the gas in the Mather-Thompson process. *Linen cloth*, notwithstanding many trials, still requires much longer time to successfully bleach than yarn. It is quite possible to bleach the cloth in a comparatively short time, but the strength of the fibre would be weakened. The following outline of the general process indicates the successive stages:

1. Liming. Boil with eight to ten per cent. for fourteen hours and wash.
2. Allow to remain in dilute hydrochloric acid (specific gravity 1.012) for four to six hours and wash.
3. Boil with resin soap (two pounds caustic soda and two pounds resin) for ten hours, followed immediately by a boiling for six to eight hours with one pound caustic soda.
4. "Grass." Expose on the fields for a week or more.
5. "Chemick." Pass through chloride of lime solution of ½° Tw. for about five hours and wash.
6. "Sour." Steep in dilute sulphuric acid 1° Tw. for two to three hours and wash.
7. Boil for four to five hours with .5 to .75 per cent. of caustic soda, wash, and
8. Expose again for four to five days in the fields.
9. Second chemick. Same as No. 5, only ¼° Tw. for five hours.
10. If necessary, rub with a soft soap between "rubbing-boards" * to remove brown spots.
11. Expose again on the grass as before.

The frequent exposure of the goods on the grass to the combined action of moisture, air, and light necessarily dispenses with a certain amount of the chloride of lime, besides allowing of a less energetic action.

3. *Jute.*—A good white on this fibre is difficult to obtain. Prior to bleaching, jute is scoured with a five per cent. solution of sodium silicate (*soluble glass*) at 70° C., washed, and bleached with a solution of sodium hypochlorite containing about one per cent. of available chlorine, made by decomposing bleaching-powder with carbonate of soda, settling, and using the clear liquid. The goods are thoroughly washed, and treated in a dilute bath of hydrochloric acid (½° to 1° Tw.) and washed, or they can be further acted on by sulphurous acid by immersing in a bath of sodium bisulphite for two to three hours, and dry. Jute can also be bleached by being worked in a solution containing one per cent. permanganate potash (calculated to the weight of its material) and exposing to the air until it becomes brown, when it is immersed in a solution of sulphurous acid and washed.

4. *Wool.*—For yarns, etc., the best known method of bleaching is "*stoving*,"—that is, an exposure of the damp goods to the vapors of burning sul-

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* "*Rubbing-boards*" are two fluted pieces horizontally placed, the upper of which is moved in an opposite direction to the course of the cloth.

phur, confined, usually, in a frame building; in the centre of the floor is mounted an iron pot in which the sulphur, in rolls, is ignited, by means of a piece of iron heated to redness and dropped in. From six to eight per cent. of sulphur is consumed, and the time required is about eight hours, but for carpet yarns and goods of a similar grade twelve hours may be necessary. The yarn is removed and well washed, the water containing, possibly, a little carbonate of soda to neutralize any sulphurous acid remaining.

For piece-goods the same process is applicable, but it requires arrangements for passing the fabric over rollers inside the sulphur-house at a uniform rate. Piece-goods can also be bleached according to two somewhat lengthy processes, embodying the sulphuring in chambers, detailed in Sansone's "Dyeing," vol. i. p. 123.

The process based upon the action of *hydrogen peroxide* is destined to become the most valuable for wool. No metal should be exposed in the wooden vats in which the bleaching is performed, and care should be taken to see that no sediment is in the water-supply pipe, all such taking up oxygen from the reagent and thus weakening it. A solution of hydrogen peroxide (equal to about one per cent., and capable of destroying six cubic centimetres of decinormal potassium permanganate solution) is made up in the vat, and this is carefully neutralized with *silicate of soda* which has been previously diluted with *warm water;* the yarn or goods is immersed and kept below the surface of the liquid by means of a wooden lattice frame. The temperature must not be above the normal. In a few hours the color of the wool will have changed to a white or nearly so, and by keeping it in a "wool white" will be obtained, when the material is lifted, and allowed to drain back into the vat, when the liquid is brought up to the original strength with fresh peroxide. The bath can be kept in use for six months. After draining, wash in water containing a trace of sulphuric acid, finally with water alone.

5. *Silk.*—The preliminary operations for treating this substance have already been mentioned. Ordinarily, silk is treated in a similar manner to wool, being hung on poles in an atmosphere of sulphurous acid for several hours (four to six), taken down and washed; or the silk can be worked in a bath of bisulphite of soda, followed by a weak alkaline wash and a final rinse. *Aqua regia* (hydrochloric acid and nitric acid, 5 : 1) of 3° to 4° Tw., and at 70° Fahr., is much used for small lots; the silk being constantly worked for about twenty minutes when the bleaching is finished. For very fine tints, the silk is entered into a soap-bath heated from 85° to 105° Fahr., wrung out, and hung in the sulphur-house for ten or twelve hours, washed in warm and cold water, and dried.

*Tussah silk* is always bleached with *hydrogen peroxide*, being immersed, as in the case of wool, for several hours, or even days. When the necessary degree of whiteness is obtained, the silk is rinsed and dried. Sansone mentions immersing the silk in strong peroxide, wringing out the excess, and teaming in a closed vessel. This method has yielded good results.

*B.* BLEACHING AGENTS AND ASSISTANTS.—*Chloride of Lime* ("Bleach-owder"), the most important agent for bleaching purposes, is produced mense quantities by acting on dry slaked lime with chlorine. It occurs ommerce as a white powder possessing a characteristic odor resembling at of chlorine, and if exposed rapidly absorbs moisture. The real strength depends upon the amount of available chlorine obtainable,—ranging between ty-two and thirty-five per cent. Solutions of the above sold under

fanciful names are met with in the trade varying in strength from five to eight per cent. "Chlor-ozone" is a product considerably used, and is essentially a solution of sodium hypochlorite.

*Permanganate of Potash* ($K_2Mn_2O_8$), although not strictly a bleaching agent, is mentioned on account of its very high oxidizing properties.

*Hydrogen Peroxide* ($H_2O_2$) is a colorless, odorless liquid obtained by the action of hydrofluoric acid upon barium peroxide in a lead-lined tank. The operation is conducted at as low a temperature as possible, and with continuous stirring; in about twelve hours the reaction is over, and the supernatant liquid drawn off and preserved. The residue, barium fluoride, is decomposed with sulphuric acid, and the hydrofluoric acid recovered. It is customary to refer to the strength of hydrogen peroxide as being of so many volume capacity, six, ten, etc.; this means that one volume of the peroxide will yield six, ten, etc., volumes of oxygen gas.

*Sodium Peroxide,* or *Sodium Dioxide* ($Na_2O_2$), is coming into use quite largely as a substitute for hydrogen dioxide, as it is in many respects more convenient to use and can be kept, when properly sealed from the air, for a long time. It is a yellowish-white powder, and can be used in alkaline or acid solution.

*Soda Ash* ($Na_2CO_3$).—This is the commercial anhydrous carbonate of soda, used principally in scouring. It is generally contaminated with varying percentages of caustic soda, sodium chloride, sulphate, etc. Its value depends on the amount of $Na_2O$ contained.

*Soda Crystals* ($Na_2CO_3.10H_2O$) is a much purer and more expensive carbonate; it contains no caustic soda, which renders it well suited to scouring.

*Caustic Soda* (NaOH).—It comes in trade in iron drums—solidly filled—or in a coarse powder. It is obtained by treating carbonate of soda with milk of lime, whereby the carbonate is decomposed with formation of calcium carbonate, when the clear liquid is drawn off and evaporated down to the solidifying point.

*Carbonate of Potash* ($K_2CO_3$) is not used in the dye and bleach works to the same extent as soda, although for silk- and wool-scouring it leaves the yarns, etc., with a better "feel," and when used in soaps, it does not cause colors to run or "bleed" to the same extent as soda. Its value depends upon the percentage of carbonate.

*Acids.*—The mineral acids are used in bleaching chiefly to neutralize alkalies, or to cause a disengagement of hypochlorous acid in the so-called "sours," and reference to their production is unnecessary. *Hydrochloric Acid* of commerce (also called *Spirit of Salt*, or *Muriatic Acid*) is yellow in color, due to impurities. The general strength is 21° Bé. (specific gravity 1.17). *Nitric Acid,* used in conjunction with the above for silk-bleaching, and largely in the preparation of some mordants, is bought with a gravity of 17.7° Bé. (specific gravity 1.140). *Sulphuric Acid* ($H_2SO_4$) is obtained by the burning of sulphur and conducting the gas into lead chambers, in contact with nitrous vapors and steam. It is a heavy, oily-looking liquid, and when pure is colorless. It is ordinarily sold at 66° Bé. (specific gravity 1.84).

*Soaps.*—The soaps employed in bleaching, etc., embrace *Tallow, Rosin,* and *Olive Oil* (for silks), although others are used, but mainly for special purposes. Reference to them has been made in the chapter on Oils and Fats. (See p. 62.) In most large establishments soap-boiling appliances are in use.

*C.* MORDANTS EMPLOYED IN DYEING AND PRINTING.—The process of mordanting is of the utmost importance, having for its object the precipitation of some substance upon the fibre which has an affinity for, and will effect a more or less complete fixation of, the coloring matter used for the dyeing. The nature of the mordanting substance used depends upon the character of the fibre, the kind of dye, and upon the effect sought; some shades require the use of several. Under ordinary circumstances *wool* is simply boiled in a solution of a metallic salt, for example, bichromate of potash ("chrome"), in the presence of a small quantity of some acid, in this case, preferably, sulphuric. Wool so treated is said to be *chromed*, and is in a condition fit to receive a black when dyed with logwood decoction. *Silk* is mordanted similarly, lower temperatures, however, being employed. If silk and wool are immersed for a time in a solution of a metallic salt, an absorption will take place, when the fibre can be washed in water, during which operation a deposition of a basic oxide will occur. *Cotton*, unlike wool or silk, has but little natural affinity for the majority of coloring matters, and of necessity must be specially prepared. It is well known that cotton has a strong tendency to combine with tannic acid, and this is made use of by steeping cotton in a solution of sumach extract, catechu, or other tannin-yielding material; if it is afterwards washed and worked in a bath of some soluble metallic salt, an insoluble compound will be formed, which *then* has the property of uniting with the dye. It is not always necessary to prepare the cotton with tannin, an immersion in the mordant, followed by an oxidation or *ageing*, being deemed sufficient.

*Substantive Dyeing* is where the coloring matter is taken up from its solution by the fibre without the assistance of any agent. Wool and silk are dyed with the coal-tar dyes in this manner, using some sulphate of soda and sulphuric acid in the case of the former, and with a soap-bath and a little acetic acid in the case of the latter. *Cotton*, when dyed with the benzidine colors, also comes under this head; it is possible a colored compound of cellulose and the base of the dye is formed. The use of salts in dyeing the above is merely to prevent a too rapid absorption of the dye by the fibre, thereby obviating uneven shades.

*Adjective Dyeing* necessitates the intervention of mordants, as above explained. Albumen, however, does not cause the formation of an insoluble precipitate on the fibre, but causes the cotton fibre to behave towards the dye in a manner similar to wool. Many coloring matters already fixed on cotton have the valuable property of serving as mordants for other dyes, a property much employed in the production of compound shades.

The following list of mordants embrace only those of prominence and in general use; exact methods for their manufacture will be found in the works of Hummel, Sansone, Herzfeld, and others.

(*a*) *Mordants of Mineral Origin.*—*Tin Mordants.*—These are first in importance to the dyer and printer. They are used in two states of oxidation, *stannous* and *stannic.* The former salts have a great affinity for oxygen, a property of considerable value as a discharge for other colors. Their solutions are colorless or nearly so, except those prepared with nitric acid, which are yellowish,—due, possibly, to an incomplete oxidation of the tin. The most prominent tin compound is *Stannous Chloride*,—when crystallized, "*tin crystals*," or as a liquid known as "*single muriate of tin*," or "*double muriate of tin*," according to the gravity. The crystals are obtained by dissolving feathered tin in commercial hydrochloric acid and evaporating; good samples contain about

fifty per cent. of metal. The impurities are iron (from the acid used), lead (from the crude metal, and from the table-tops on which the crystals are drained), and sometimes copper. The "muriates" are nothing more than the mother-liquor from the crystals, diluted for "single" to 60° Tw. (specific gravity 1.3 = about thirty-eight per cent. $SnCl_2.2H_2O$) and for "double" to 120° Tw. (specific gravity 1.6 = about sixty-one per cent. $SnCl_2.2H_2O$). The above are chiefly used in connection with the natural coloring matters.

*Tin Spirits*, owing to the advent of the tar-colors, are much less used than formerly. Their composition was exceedingly variable, consisting usually of stannous chloride, with or without additions of sulphuric, oxalic, tartaric, and nitric acids, and they bore such names as *Amaranth Spirit*, *Yellow Spirit*, *Finishing Spirit*, etc. "Stannous Nitrate" (nitrate of tin) is essentially a solution of tin in nitric acid, the chemical composition of which is doubtful. "*Tin spirits*" is a collective name for a long list of *stannic* compounds, made, usually by the dyer, from hydrochloric and nitric acids, sodium and ammonium chlorides, etc. Their use is gradually going out. *Stannate of Soda*, or *Preparing Salt*, is used in cotton- and woollen-printing; its value depends upon the amount of stannic oxide contained.

*Alumina Mordants.*—*Sulphate of Aluminum*, also known as *Patent Alum*, does not find much application in the dye-house, but is considerably employed in the preparation of other alumina compounds which are, being much more economical than potash or ammonia alum. It is obtained from the mineral bauxite, and from cryolite. The brand manufactured for paper-makers is the purest, containing but little or no iron. By the addition of alkaline carbonates the normal aluminum sulphate is changed into a basic sulphate which yields alumina to the fibre more readily. Their application to cotton is followed by a treatment with ammonia or soap to fasten the alumina more fully, to wool generally with cream of tartar, and to silk by immersion overnight in the solution, followed by a washing, which causes the formation of a *basic* salt. *Aluminum Acetate*, or "Red Liquor,"—so called from the original use to which it was put, dyeing reds,—is obtained by the double decomposition of aluminum sulphate and *calcium* or *lead acetate* in the proper proportions, and using the supernatant liquid. Professors Liechti and Suida, and Köchlin have conducted elaborate researches into the action of the aluminum compounds as mordants, and their results have thrown much light upon the whole subject of mordanting. *Sulpho-acetate* of *Alumina* is obtained when an insufficient quantity of the acetate (lead or calcium) is added to decompose the alumina salt, and this forms the *red liquor* of trade. Ordinarily, the solutions have a dark-brown color and are characterized by a strong pyroligneous odor. The cotton-dyer and printer, especially the latter, make considerable use of this mordant, for reference to which, see p. 478. The remaining alumina compounds—viz., *chloride*, *nitrate*, *hyposulphite*, *oxalate*, etc.—are but little used, chiefly in calico-printing for alizarin shades.

*Iron Mordants.*—Like tin, iron is employed in two states of oxidation, —*ferrous* and *ferric*. *Ferrous Sulphate* ($FeSO_4.7H_2O$), *Copperas*, or *Green Vitriol*, occurs as a by-product from several chemical processes, and is much used in cotton-dyeing, and in the preparation of iron mordants. *Ferrous Acetate*, also called *Pyrolignite of Iron* and *Black-iron Liquor*, is manufactured similarly to the acetate of alumina, or by dissolving scrap-iron in crude acetic acid. It is applied in the same general manner, and to the same fibres, as the alumina compound. The remaining iron mordants are the

*Nitrates* and the *Nitro-sulphates.* The former are obtained by dissolving scrap-iron in nitric acid to the proper degree of saturation, and the latter, by treating copperas with nitric acid; as an iron mordant for black on silks this latter is probably the best, from the fact that the iron exists in both states of oxidization.

*Chromium Mordants* comprise among the most important *Bichromate of Potash and Bichromate of Soda,* both being products obtained from chromite. The former is well crystallized, the latter is quite deliquescent, frequently becoming fluid; in price it is cheaper than the potash salt, and yields the same results. It is a valuable wool mordant, and is also much used as an oxidizing agent. *Chrome Alum* (Potassium Chromium Sulphate) is a residue from the manufacture of alizarin, and is employed as the basis for producing many of the chromium mordants. *Chromium Acetate* is obtained by double decomposition of lead acetate and chromium sulphate, and in commerce it is found of about 30° Tw. (specific gravity 1.15). It is used in printing. Other compounds used are the chloride, sulphate-acetate, and alkaline chromhydrate solution.

*Copper Mordants* are well represented by the *sulphate* (*blue-stone*) and the *nitrate. Sulphate of Copper* is used in dyeing blacks, mostly in conjunction with other mordants, and, owing to its cheapness, is used for the production of nearly all the copper compounds. *Nitrate of Copper* is easily prepared by dissolving scrap-copper, not brass (as free from lead and solder as possible), in nitric acid, and diluting to 1.4 specific gravity. In cold weather good crystals are obtained, but they absorb moisture very rapidly. The *sulphide* and *acetate* find little application except in special cases.

*Antimony Mordants.—Tartar Emetic* (Antimony Potassium Tartrate) is the best known of this group, and is much used for fixing tannin in cotton-dyeing. *Oxychloride of Antimony* is another form, used for the same purpose. It is sold as a concentrated solution, made by dissolving metallic antimony in a mixture of hydrochloric and nitric acids and diluting very cautiously to 80° Tw. (specific gravity 1.4). Of late, double fluorides of antimony and potassium, and of sodium have been brought on the market as substitutes for tartar emetic. They are well crystallized, easily soluble, and cheaper. The mode of application is the same as for other antimony salts.

Other mordants besides those above mentioned are used, but not as extensively, and enough has been said to indicate their general nature; under the operations of dyeing the special uses to which they are applied will be mentioned.

(*b*) *Mordants of Organic Origin.—Tannin* (Tannic Acid) is now produced in large quantities of exceptional purity for use in the arts, and offers to the dyer a convenient mordant in place of many tannin-yielding substances, which, however, still hold their position on account of other properties. Tannin is much used by the cotton-dyer, and is applied generally in two ways: first, by *steeping*, and, second, by *padding*. For silk, tannin is extensively used in the production of blacks, and also for weighting. *Catechu*, or *Cutch* (see p. 449), is used in a similar manner to tannin, for the production of browns, drabs, blacks, and other shades, in combination with bichromate of potash, copper, iron, etc. Catechu is bought in mats weighing about one hundred and fifty pounds, and also as "cutch extract," or "prepared cutch," made by dissolving the crude cutch, straining from sticks, stone, etc., and evaporating to about 51° Tw. It is used for wool and for silk. *Sumach* (Shumach) is used in the dye-house in the ground

state, and as an extract, which is, in some instances, grossly adulterated. *Nutgalls*, rich in tannin, find extensive application both in dyeing and printing, especially when light shades are to be fixed. They occur whole, "crushed," and as an extract, which comes usually of two qualities. *Myrobalans, kino, divi-divi*, etc., are also employed.

*D.* Dyeing and Printing.—1. *Dyeing.*—The apparatus used by the dyer consists of vats, kettles, cisterns, etc., and are ordinarily constructed of wood, although they may be also of metal, and even stone. Their capacity, in case of woollen yarn, is such that they can conveniently accommodate a hundred pounds of material, although the sizes vary according to circumstances. Wooden kettles are heated by a copper steam-coil inside and on the bottom, and are provided with a water-supply pipe, and a lifting plug-valve for emptying. Metal kettles are preferably heated with steam by a coil or double bottom. Open fires are used in England and Europe to some extent, but in the United States very rarely, if at all. The shapes of the vat or kettle vary with the material to be dyed. For cotton, wool, and silk yarns they are mostly rectangular, and of varying depth, for loose material, mostly circular; in the case of indigo-vats for yarns, they are wine-pipes stood on end; this gives a great depth of liquid with a minimum of exposure. In hand-dyeing, the yarn is hung, and worked on sticks laid across the top of the kettles; piece-goods are worked by means of a movable winch, sliding as occasion requires from one end of the kettle to the other, taking care to guard against twisting the fabric. Loose material is either dyed as such in circular tubs, or else is tied up in bags; and warps are passed over a series of rollers immersed in the dye-liquor, and then between squeezing or nipping rollers.

Of primary importance in successful dyeing is a regular supply of pure water, and in the absence of this, various means must be resorted to to purify the water at hand, which may be contaminated with sewage, which may not render it unfit for use, or else it may contain *lime* or *magnesia*, usually as bicarbonates, which are soluble, or it may have *sulphates* or *chlorides*. Iron (when present it is as a bicarbonate) is very objectionable, and, for some operations, prevents the use of the water. Water which has flowed through limestone regions will invariably be *hard* from the *lime* dissolved, and that which flows or is pumped from granitic regions will be *soft*, due to the absence of lime, etc. In the event of water having suspended matter, this can be easily removed by suitable filtration, but if other impurities are present, chemical purification should be resorted to. A *hard water* is one which has bicarbonate of lime or magnesia dissolved, this solution being really a dissolving of *carbonate of lime* in carbonic acid contained in the water; besides the above, it may contain in solution *sulphates* of lime or magnesia. A water containing no sulphates, if boiled, would lose its hardness by the *bi*carbonate splitting off into carbonic acid gas and carbonate of lime or magnesia, which would be precipitated (temporary hardness); if sulphates were present, the boiling would have no effect on them (permanent hardness). A *soft water* is one containing no such impurities.

*Chemical Purification* for water embraces several processes, notably Dr. Clark's: decomposing the bicarbonate with a clear solution of calcium hydrate, by this means the excess of carbon dioxide is combined with the lime added, which is precipitated and removed by settling. Only the temporary hardness is removed. The *Porter-Clark* process is similar to the above, with the exception that the precipitates are removed by the water

being passed through a filter-press. *Caustic Soda* is also used as a purifying agent, which removes both the temporary and permanent hardness. The water will then be slightly alkaline. Alum and sulphate of alumina are extensively used in water purification for dyeing purposes. The alumina compound, if added to a water in suitable quantity, is completely eliminated by combining and separating with the impurities.

*Solution of Coal-tar Colors* requires a little care, because if imperfectly done the yarn or fabric will be spotted or striped: effects exceedingly difficult to remove. The colors are dissolved readily in warm water; some may require almost a boiling temperature, while others are injured when highly heated. They ought never be over a direct fire. In all cases it is well to strain them through felt.

*Cotton-dyeing.*—Two operations are necessary, mordanting and dyeing, except in indigo-dyeing, where no mordant is required, and in the application of the benzidine and primuline colors. In the case of *raw stock*, the operations are conducted in large circular or rectangular vats, heated as previously described, and provided with the necessary inlets and outlets for water, the outlet being covered with a gauze screen in order to keep the loose material from stopping it up. The material is "poled" or worked by long-handled rakes or by mechanical means. The *washing* can be done in a similar apparatus, or in one similar to a wool-scouring machine. For *yarns*, besides the open kettles mentioned on the preceding page, many mechanical devices are in use, and are well suited where large quantities of material are to be worked to one shade, but in cases where different shades are to be produced, hand-dyeing cannot be excelled. For *warps*, the apparatus referred to on p. 456 is used; it can be made with two or more kettles, so that the warp can pass through two or more different solutions. This arrangement is admirable for mordanting, dyeing, and washing, or in the event of using the primuline colors, requiring rapid treatment. The several baths can be maintained at different temperatures.

*Cloth-dyeing Machinery.*—The vats are either iron frames and wood or all wood, in some places small enough to stand on the floor of the dye-house, in others they must be sunk below that level, in all cases surmounted with a hand or power winch for working the pieces. *Drying* is accomplished by wringing cut the yarn, centrifugating, and hanging on wooden sticks in a "dry-room," or in the case of piece-goods, squeezing through rollers, centrifugating, and carefully arranging on sticks as above.

*Application of the Natural Coloring Matters.—Indigo.*—This dye is always applied in the cold, and by any of the several "vats" now known, among which the *lime and copperas* may be mentioned. This vat, or series (usually ten), is made up in various proportions, the amount of ground indigo ranging from thirty to thirty-eight pounds, copperas, fifty to eighty-five, lime, eighty to ninety. The vats being filled with water, the lime is added, followed by the ground indigo and the copperas, raking the whole up occasionally until the indigo has been reduced, which is known by the olive-colored appearance of the liquid. A good working vat is known by peculiar blue streaks or veins which appear when it is raked. The dyeing is performed by dipping the wetted yarns in the oldest (weakest) vat, then squeezed out, placed aside to oxidize, and passed through the next, and so on until the proper depth of shade is reached, the whole operation being conducted systematically. The lime which is precipitated on the yarn is removed by means of a weak acid and washing. Piece-goods are dyed in a

similar solution by fastening the material to a large frame, which is dipped and re-dipped until the proper shade is obtained, or, in case of warps, also by passing over immersed rollers in a large vat, and finally over rollers exposed to the atmosphere; this is particularly suited for light shades.

*Zinc-powder* is much used in indigo-dyeing, supplanting copperas; for forty pounds of indigo about twenty pounds of zinc-dust are used. This vat is more economical than the preceding. Other vats are also employed, —viz., *hydrosulphite, German soda vat, urine*, etc., but those detailed indicate sufficiently the character of the operation.

*Logwood.*—This dye-wood is used in the form of liquid or solid extracts, and as chips, and mainly for the production of blacks. The cotton is mordanted in a cold solution of acetate or nitrate of iron, squeezed, and the iron precipitated on the fibre by passing through a solution of carbonate of soda, and boiled in the logwood-bath; or the cotton is allowed to steep in a solution of tannin (sumach, galls, etc.) for several hours, then worked in dilute iron solutions as above,—this produces a tannate of iron,—followed by a passage through weak lime-water, and dye in a separate kettle. Acetate of alumina can be used with the iron, somewhat modifying the shade. A "chrome black" can be obtained by dyeing in a single bath of bichromate of potash, hydrochloric acid, and logwood; many modifications of this process are known. Gray shades can be obtained by first working in logwood, and afterwards in the copperas or bichromate of potash baths.

Of the *red dye-woods* little need be said, as their practical utility in dyeing is on the decrease; their coloring matters are fixed in the usual manner with tin, alumina, or iron mordants. Of the yellows, *Quercitron Bark* and *Turmeric* are the most important; the former, used chiefly as an extract, is available for the production of greens, etc., in combination with other coloring matters. Turmeric is applied directly to the cotton by working in a plain bath, the color having a natural affinity, although it is not very fast.

*Application of the Artificial Coloring Matter to Cotton.**—In this section only the individual colors will be referred to, any attempt to discuss the production of *shades* by compounding would be beyond the scope of this publication.

*Fuchsine* is dyed upon tannin-prepared cotton, or upon cotton that has been worked in small quantities at a time in a bath of ten per cent. of neutral soap or Turkey-red oil, followed by an immersion in a warm bath of two hundred and fifty gallons water and one gallon acetate of alumina (9° Tw.). Work half an hour, wash, pass through a soap-bath for fifteen minutes, wash, squeeze, and dye. The color is added in successive portions until the required shade is obtained. *Safranine* is dyed upon a tannin mordant, or the tanned material is worked in a 3° Tw. bath of stannous chloride for an hour, washed, and passed through a two per cent. soap solution, and dyed at 140° F. *Methyl and allied Violets* can be dyed upon tannin as above, or pass the untanned cotton through a one per cent. olive-oil-bath, squeeze, and dye at 100° F., or with the assistance of acetate of tin, or with alum and soda. The *basic greens*, including *Victoria Green, Methyl Green, Brilliant Green*, etc., are easily dyed upon cotton in the ordinary manner with a little (.5 per cent.) acetic acid.

The *Eosins*, with *Phloxin*, etc., are dyed in several ways: first, by pass-

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* Reference has been made in the preparation of this and subsequent sections on its applications to several of the published trade circulars issued by the coal-tar color manufacturers, and also to information from private sources.

ing the cotton through a two per cent. soap-bath, followed by an immersion for two hours in from two to three per cent. acetate of lead, washing well, and dyeing, cold, with a little acetic acid; or, second, by working in a dye-bath with eight to ten per cent. sulphate of soda, or the cotton can be worked in 5° Tw. bath of stannate of soda for an hour, worked for thirty minutes in a ten per cent. alum solution, rinsed, and dyed cold. *Rhodamin* is dyed on acetate of alumina exactly as for fuchsine. *Brilliant, Cotton,* and *Soluble Blues.* The cotton is tanned and dyed with five per cent. alum and one per cent. soda; or the tanned cotton can be worked in a 3° Tw. stannous-chloride bath for an hour, rinsed, and dyed at 150° F. If light shades are to be produced, work the cotton in a five per cent. soap-bath for an hour, squeeze, and work in a three per cent. tannin-bath, wring out, and dye with the assistance of tartaric acid and alum. *Victoria Blue.* Cotton is mordanted with tannin; dye with one per cent. acetate of alumina. *Methylene Blue.* This is an exceedingly valuable color to the cotton-dyer, as with it he can produce indigo shades. The cotton is mordanted with twenty-five per cent. sumach at 160° F. Give several turns, and allow to steep ten hours, wring out, and work for twenty minutes in two and one-half per cent. tartar emetic, wash, and dye in a bath prepared with acetic acid (three per cent.) at 75° F., gradually raising the temperature to 160° F. *Crocëin Scarlets* are dyed on cotton by working the untanned yarn in stannate of soda, wring, and pass for half an hour through sulphate of alumina, rinse, and dye. Cotton can also be dyed by passing first through stannic chloride, and then through acetate of alumina. Dye cold, or dye direct, with sulphate of alumina. *Auramin,* of considerable value, is dyed in the same manner as methylene blue. *Bismarck Brown* and *Chrysöidine.* Dye same as safranine; temperature 100° F. *Induline* and *Nigrosine.* Dye in same manner as for the cotton blues. *Paraphenylene Blue* is dyed upon tin or antimony, and tannin. The shades produced are very dark, and extremely fast; treated with bichromate of potash, the shade closely imitates, and is faster than, indigo. The substantive colors of the Congo and parallel groups are exceedingly valuable, for the reason that they are easily dyed upon unmordanted cotton, and that they are of exceptional fastness. The several *Congos, Benzo- and Delta-purpurin,* and *Rosazarin,* are dyed with two and one-half per cent. soap and ten per cent. sulphate of soda, or phosphate of soda, boil for one hour. *Hessian Purple* is dyed at a boil for half an hour with ten per cent. common salt, followed by a passage through dilute soda. *Chrysamin* is dyed with ten per cent. sulphate of soda and two and one-half per cent. soap at a boil. *Hessian Yellow* is dyed with ten per cent. of salt and a little Turkey-red oil. *Brilliant Yellow* and *Chrysophenin* are dyed with ten per cent. salt and two per cent. oxalic acid, work half an hour, squeeze, rinse, and dry. *Azo Blue,* and *Benzoazimine, Heliotrope,* etc., are dyed with ten per cent. sulphate or phosphate of soda and two and one-half pounds of soap, let stand, and skim the surface, add the dye, boil, and put in the yarn, and work for an hour, *boiling,* rinse the yarn, and dry at as low a temperature as possible. *Indigo shades* from *Benzoazimine* are obtained as above, but for every one hundred parts of color add three parts *Chrysamin.* All the benzidine dyes act as mordants for a very large number of other colors, no other fixing agent being required.

*Aniline Black.*—This color is produced directly upon the fibre during the dyeing by means of aniline oil in the presence of oxidizing agents; to obtain good results it is necessary that the oil used should be as pure as pos-

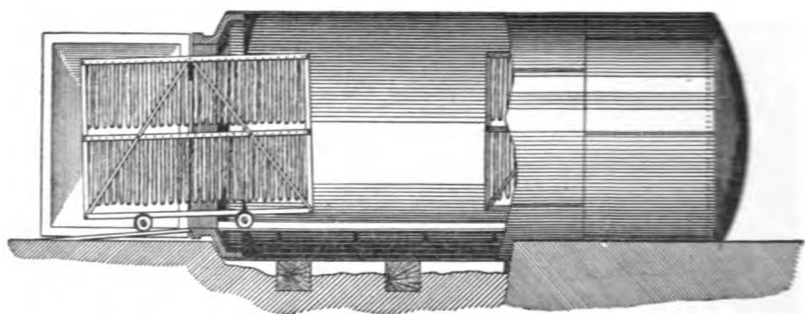
sible. Two methods are in general use,—*warm* (Grawitz patent) and the *cold*. In the former method, two thousand four hundred litres of water, thirty-two kilos. hydrochloric acid, sixteen kilos. bichromate of potash, and eight kilos. aniline oil are taken. The acid and aniline are each diluted with water and carefully mixed, the solution thus obtained being added to the main volume of water. The bichromate of potash is previously dissolved and added after the aniline. Immerse the cotton, and work for three-quarters of an hour in the cold, and then gradually raise the temperature to 60° or 70° C. In the cold method take eighteen kilos. hydrochloric acid, eight to ten kilos. aniline oil, twenty kilos. sulphuric acid, 66° Bé., fourteen to twenty kilos. bichromate of potash, and ten kilos. copperas. This bath is made up similarly to the previous one, with the exception that much less water is used. Aniline salts in solid form are often used instead of aniline oil and acid. The yarn is worked in one-half of the materials for an hour or so, after which the remainder is added, and the operation carried on for about one and a half hours longer, followed by a washing, and a boiling in a soap solution. In either case, the cotton after dyeing is subjected to a further oxidization with bichromate of potash, copperas, and sulphuric acid,—this having a tendency to prevent greening. Chlorate of soda is used considerably as an oxidizing agent in the dye-bath. Vanadium chloride, or vanadate of ammonia, has been recommended to be used with a chlorate in place of bichromate of potash; the proportion of the vanadium salt being to the displaced bichromate as 1 : 4000. Another method is to produce the aniline black in powder form, purify it, liberate the base, which is dissolved in sulphuric acid, poured into water, and the precipitate formed thereby dissolved in caustic soda. This is reduced as in the case of indigo, and dyed in a similar manner.

*Alizarin-dyeing, Turkey-red Process.*—J. J. Hummel, in his "Dyeing of Textile Fabrics," 1886, p. 427 *et seq.*, details the *emulsion process*, which need not be described here. It may be stated, however, that beautiful results have been obtained from its use; the yarn passes through fourteen operations, as follows: boiling in soda and drying, worked in an emulsion of oil, dung, and carbonate of soda; passed through the previous process twice again; worked four times in carbonate of soda, steeped in water, and in carbonate of soda, sumached, mordanted with alumina, dyed with alizarin (ten per cent.), sumach, and blood, cleared with carbonate of soda, final clearing with soap and tin crystals. To finish the dyeing requires about three weeks, but a real Turkey-red is produced. Except for some grades of goods, it is doubtful whether such a lengthy process would be profitable.

The following scheme of a process represents the type of a reasonably short one; it is well to remember that it can be modified to a considerable extent without altering its product. It is used in several establishments essentially as given. Boil the cotton for two hours in a 1.04 specific gravity solution of caustic soda, wash well in water, dry, and work in seven to ten per cent. solution of Turkey-red oil, squeeze, dry at about 115° to 120° F., steam in a chest, mordant with acetate of alumina (red liquor) at 80° Tw., and dry as before; work for an hour in a hot bath of five pounds of dung and eight to ten pounds of chalk, followed by a good wash, and pass to the dye-bath, made up of eight per cent. of alizarin, two per cent. Turkey-red oil, and about one per cent. of ground sumach, or equivalent in pure extract. Enter cold, and slowly increase the temperature to and maintain it at 160° F. for over half an hour. Dry, and steam in

the chest as above. The final operation is a soaping with carbonate of soda and stannous chloride as in the above emulsion process.

An almost unlimited number of processes could be given, but it is hardly necessary, the principle remaining the same in every case. For full information reference is made to Hummel, Sansone, and Knecht, Rawson, and Löwenthal. The apparatus used for alizarin-dyeing is not special, with the exception of the machines for "padding," the material to be dyed with the oils and for working in the liquors; the most important is the steam-chest, which is essentially a large cylindrical wrought-iron drum with cast ends, one of which is provided with a well-closing door. The chest, or *steamer*, is provided with a steam-supply pipe, gauge, and safety-valve. The yarn or cloth is hung on sticks supported on rods inside, or, as shown in Fig. 124, mounted on iron carriages. Some chests are so built that the

Fig. 124.

yarn contained can be turned while closed and with the steam pressure on, which seldom exceeds four or five pounds.

*Ingrain Red*, a color obtained from *primuline* or *polychromine*, is for some purposes a perfect substitute for Turkey-red, being fast to light, soap, and acids. Primuline is dissolved in warm water, common salt or sulphate of soda added, and the yarn worked in the bath until a good full yellow is obtained, when the material is washed, and immersed in a cold solution of nitrite of soda slightly acidulated with either hydrochloric or sulphuric acid, this causes a diazotizing of the yellow color, with the production of an unstable orange shade; the yarn is lifted out, washed rapidly, and at once dipped in a warm solution of *β-naphthol* in caustic soda, when a deep-red color is developed. The yarn is worked for a while, and afterwards well washed in water. If *phenol* or *resorcin* is substituted for the β-naphthol, a fast *yellow* and *orange* color, respectively, will be obtained. The diazotized yarn is very sensitive to the light, if it is not in a reasonable time developed, no color will be obtained; this fact is at the present time experimented upon with a view to its possible use in photography.

A more recent and still better substitute for Turkey-red is the azo-para-nitraniline obtained by diazotizing para-nitraniline C and developing with β-naphthol and red developer C. The cotton yarn is preferably first impregnated with the caustic soda solution of the developer, made with the addition of castor oil soap, and then put in the diazotized solution.

*Linen*.—The uses to which fabrics made of this fibre are put demand colors that shall be fast to washing, light, and air; this requirement being satisfied

by alizarin and indigo. The coal-tar colors, as a rule, are not applied, although they can be by treating the fibre in the same manner as cotton.

*Jute*, owing to its peculiar chemical structure, does not require any mordanting; all basic colors can be applied by simply boiling in a neutral bath. Some scarlets and a few of the acid colors are fixed with the assistance of a little acetic acid in the dye-bath, sometimes with a little sulphuric acid and alum.

*Wool-dyeing.*—*Raw wool* is dyed in the same manner as raw cotton, in open kettles, or in machines made for the purpose. *Woollen yarn* and *cloth* are similar in their manipulation to cotton, the apparatus being in both cases nearly the same. Dyeing-machines for carpet yarns are coming slowly into use, several forms being capable of handling a large quantity in comparison with hand labor.

Some classes of goods, *i.e.*, plushes, have cotton backs,—these being previously dyed in the hank and warp and then woven,—the face, or pile, is afterwards dyed the proper shade, care being taken to select such colors as will have no modifying effect upon the cotton color. For this purpose cotton dyed with aniline black, indigo, or alizarin are best suited.

*Natural Coloring Matters applied to Wool.*—*Indigo*, as extract, is easily applied, and is extensively employed in the production of light and dark shades by simply boiling the wool in a bath made up with the color, sulphuric acid, and sulphate of soda. If other coloring matters are to be used in connection with the above for the production of compound shades, a *neutral* extract had better be used, and the dyeing done without the above acid. *Wool* is dyed in a *vat*, where exceptionally fast and full shades are demanded, especially for army cloth. *Loose wool* is dyed in the so-called *fermentation-vat.* The wool being kept below the surface of the liquor, worked about by means of long rakes for a sufficient time, and taken out and put in large cord bags, or placed upon rope screens to drain and oxidize. It is finally dipped in very dilute acid to remove soluble impurities, well washed, and dried. *Woollen yarn* is worked in vats exactly as in the case of cotton. *Cloth* is worked in the vat below the surface of the liquid, by means of poles with hooks. The best indigo-dyed cloth is that made from wool which has been previously dyed in the raw state,—*dyed in the wool.*

*Logwood.*—This dyestuff is the real base of the blacks upon wool, the most generally followed method being with bichromate of potash as a mordant. Boil the wool in a bath of three per cent. bichromate and one per cent. sulphuric acid for an hour, lift out, rinse, and boil in a bath (made with a decoction of about forty per cent. chipped logwood) for an hour, lift the wool, and add a little extract of fustic, continue the boiling for a half-hour. This will yield a rich black. Various modifications are practised, depending upon the exact shade desired. To prevent a "greening," or development of greenish tinge on exposure of the goods to the light, a coal-tar color, such as "cloth red," is dyed on first, so as to neutralize the effect of the green shade which may form. For cheap work "*one-dip blacks*" are used,—these consist chiefly of a mixture of logwood and a mineral mordant, iron or copper. Wool can be mordanted with copperas, copper, and cream of tartar, etc., followed by dyeing in the logwood, or it can be worked in the logwood first, followed by a "development" in a bath of ferrous sulphate of iron and copper.

*Logwood Blue*, for some kinds of work, is an excellent substitute for indigo, full shades being obtained by direct dyeing, or by dyeing upon a

light indigo bottom. Hummel gives the following method. Mordant the wool for one to one and a half hours at 100° C. with four per cent. of aluminum sulphate, four to five per cent. of cream of tartar; wash well, and dye in a separate bath for one to one and a half hours at 100° C., with fifteen to thirty per cent. of logwood and two to three per cent. of chalk. The addition of a little alizarin or tin crystals to the bath at the termination of the dyeing will cause the appearance of "bloom," peculiar to indigo.

The *red woods* are fast losing ground, although before the introduction of the artificial scarlets and cardinals they were much used. *Madder*, likewise, has been superseded by artificial alizarin. Wool was mordanted for browns with bichromate of potash as for logwood; for *reds*, mordant with alum, or sulphate of alumina, with cream of tartar (argols), and boil. Tin crystals and tartar produce a reddish-yellow. These colors were not brilliant, but the value of them depended upon their fastness. The use of *Cochineal* is mainly for the scarlets obtained therefrom. The wool is mordanted with tin crystals and cream of tartar, washed, and dyed in a bath with five to ten per cent. of cochineal (ground) for an hour. Another method is to boil the unmordanted wool in a bath of cochineal, tin crystals, and potassium oxalate for an hour. For *scarlets* with a bluish cast (*crimsons*) the wool is mordanted with aluminum sulphate and cream of tartar, or the wool can be mordanted in a bath containing tin crystals, tartar, and aluminum sulphate, followed by the dyeing in a separate bath. Copper, or iron, as a mordant will produce dark shades, and as impurities in the dye-baths will have a saddening effect upon the color obtained. *Fustic* is largely used in wool-dyeing, chiefly, however, in combination with other colors,—*i.e.*, indigo extract to produce greens, olives, sages, etc., and always upon mordanted wool, using tin crystals, sulphate of alumina, bichromate of potash, iron, and copper. *Quercitron Bark* is used for the same purpose as fustic and under the same conditions. *Flavin*, a production of the latter, is used in the same manner, its chief advantage is that it is much more concentrated. *Archil* (*Orchil*) as "extract," liquor, or paste is extensively used in the dyeing of carpet yarns; it is applied by simply boiling the yarn in a bath with the color, sulphuric acid, and sulphate of soda. It is exceedingly difficult to remove from yarn once dyed with it; a process which will economically accomplish this is much sought after by manufacturers.

*Application of the Coal-tar Colors.*—As a general rule, it may be stated that nearly all the soluble artificial colors can be dyed upon wool without any special treatment, by boiling in a bath with ten per cent. of sulphate of soda and two to four per cent. of sulphuric acid. A few exceptions may be given: *Alkali Blue* (Nicholson's Blue). The color is dissolved in carbonate of soda, poured into the dye-bath, the wool entered, and the temperature raised to the boil, keep boiling for a while, lift, rinse well, and immerse in a bath of very dilute sulphuric acid, when the color will be at once developed. The *Violets* (Hofmann's, etc.) are dyed neutral, or with a little soap. *Methyl Green* is applied to wool with borax, after having been mordanted with hyposulphite of soda and hydrochloric acid. *Auramine* is dyed both neutral and acid. The *Indulines* are dyed neutral, and then boiled in dilute sulphuric acid. *Galléin* and *Cœruléin* are dyed upon wool mordanted with potassium bichromate and a small quantity of acetic acid. The application of *Alizarin* to wool is exactly as for madder, the general mordant being sulphate of alumina and tartar for *reds;* tin crystals and tartar for *orange;* potassium bichromate and sulphuric acid for *red-*

*browns;* iron and tartar yield *violet;* and copper, shades of *brown.* The addition of a little lime to the dye-bath is necessary in case none is naturally present in the water.

*Nitro-alizarin* (Alizarin Orange) produces with several metallic mordants, applied as above, a range of shades, which have not reached commercial importance. *Alizarin Blue* is dyed upon a chromium mordant, and yields a durable blue, of some value,—for wool, the price of the dye is against it.

Alizarin blues, such as *Alizarin Blue H R*, which are made by combining alizarin or a derivative of the same with a base, such as aniline, give various fast shades, and are dyed nearly the same as the older alizarin blue and alizarin blue S, except that the bath may be exhausted with very little or no acid.

The *mineral* colors are dyed upon fibres through the decomposition of metallic salts, for example, to dye *Prussian Blue*, the wool is worked in a bath of red prussiate of potash and sulphuric acid, and gradually brought to a boil, squeezed, rinsed, and dried.

*Silk-dyeing.*—Silk has a great affinity for the coal-tar colors, with which it can be dyed without any mordant, although it is customary to employ a soap-bath (boiled-off liquor) with or without the addition of a weak acid, usually acetic. If soap is not used the colors will appear streaky or spotted. For ribbons, fancy dress goods, plushes, etc., the above colors are solely employed, with the possible exception now and then of recourse to some natural coloring matter, the use of the latter being almost restricted to logwood for blacks and modified shades, including browns. Silk is dyed in skeins or hanks, warps, or pieces, this latter including plushes. The machinery is of the simplest kind, embracing the kettles, with and without winches, washing-machines, etc., and need not be especially described.

Silk is not dyed with indigo (vat process), but indigo shades are obtained by using indigo-carmine. Black is obtained by several processes. Work the silk in acetate of iron and wash, then in a warm soap solution, followed by an immersion in ferrocyanide of potash, washed, and worked again in the iron-bath, rinsed well, and steeped in a solution of catechu or gambir for ten or twelve hours and washed. This preliminary process is necessary in order to insure a good result if systematically carried out and not forced. The material is dyed in a logwood decoction containing soap.

To obtain heavily weighted goods, the process of dipping in iron solution and then in tannin-containing liquors is often repeated several times. A method giving excellent results, and which is considerably used, is as follows. Wash the goods, and pass through a bath of nitrosulphate of iron, wash, and then through a solution of carbonate of soda. These two operations are repeated several times, each time causing the precipitation of more iron upon the fibre, and consequently "weighting" the silk. Work for some time in a bath of ferroprussiate of potash and then in a bath of catechu, followed with a little "muriate of tin" or tin crystals, wash, and transfer to the logwood-bath, which may contain a little extract of fustic to modify the shade required, then to a soap-bath. Every locality is not suited to black silk-dyeing on account of impurities in the water, careful purification of which is a special requisite. *Seal plushes* are dyed, first in a dye-bath in the ordinary manner, a dark-brown shade, followed by the application of a black, blue-black, or other color, in the form of a paste thickened with starch, gum, or other medium. The application of

this being done on a machine provided with revolving brushes, and so regulated that only the *tip* or face of the piece of goods is coated. One important feature in plushes of this character, and also in other kinds of silk goods which have been heavily iron-mordanted, is that the natural lustre of the fibre is somewhat destroyed; this is supplied by means of a paste mixture of vegetable oils made into a paste with starch or other substance, applied as in the case of the *tip*, and steamed in an apparatus similar to that used for alizarin red (p. 488). The oil, usually a definite amount, is absorbed by the silk fibre under the influence of steam, imparting a permanent lustre. The goods, when removed from the steamer, are washed to remove the starch, excess of oil, etc., when they are ready for other operations.

The weighting of silk is accomplished by the use of iron, as explained above. This, however, is suitable for dark shades only; for light shades, tin in combination with sodium phosphate and soap is used.

A class of fabrics similar to plush, but with the *pile* of two or even three colors, much used for carriage-robes, etc., and dyed to imitate the skins of animals, are prepared in the following manner: The material (cotton-black and silk *pile*, the former previously dyed a fast color) is dyed, say a brown, in the ordinary manner; upon the fibre is then applied a discharge made of stannous chloride solution and permanganate of potash. This is so controlled that only one-half of the fibre is acted upon. When the effect is produced the excess is washed off, rinsed, dried, and, if necessary, a *tip* is applied, which only dyes the very face of the pile. In this manner three colors are obtained on each thread of the face. After treating as above, the whole may be dyed a very light shade, thereby producing modified effects.

The artificial coloring matters are applied to silk as previously stated. *Nicholson's Blue* (Alkali Blue) is applied as directed for wool, and seldom for the production of mixed shades. *Picric Acid* is much used for compounding, especially for greens, faster colors can be obtained by using naphthol yellow and indigo-carmine. The *Eosins* yield beautiful colors, and are applied in a soap-bath followed by a brightening in dilute acid. The *Azo* dyes are applied with a neutral soap-bath.

The use of *Alizarin* with silk is only in cases where fastness is of more importance than brilliant shades. *Alizarin Black* is being much used in dyeing *mohair goods* (astrachans), and is applied in the ordinary manner.

*E.* PRINTING TEXTILE FABRICS.—A brief outline of the more important "*styles*" in use is all that will be attempted in this section, from the fact that the subject is too extensive to enter into the details satisfactorily. The processes in general are conveniently divided into two main groups, differing in the manner of applying the colors,—namely, *Direct Printed Colors*, *Dyed Colors*.

*Direct Printing* is done by mixing the desired color with the proper fixing agents and applying directly to the fabric by means of blocks engraved with the design, or in a machine provided with a cylinder upon which the design is likewise engraved; for each color to be applied a separate cylinder is needed. From the above it is obvious that the color so applied will appear only on those portions of the fabric brought in contact with the design.

*Dyed Colors* are obtained by printing different mordants upon the cloth, as above, and fixing as for ordinary cloth, and then dyeing the whole, or,

by printing upon the cloth *resists*, substances which will prevent the dye from becoming fixed at those places so printed, or, again, by dyeing the whole piece first, and then producing patterns or designs by means of substances which will destroy the ground-color whenever brought in contact; these substances are called *discharges*. This broad definition is deemed sufficient for the purpose intended; the principle of each style will be apparent upon following the methods hereafter given.

The operations conducted in a print-works embraces as a preliminary *bleaching*, the details of which are referred to on p. 473. Then the preparation of the colors, which is always done in copper pans mounted in such a manner that they can be emptied easily, and that their contents can be boiled by steam, and cooled by water, facilities for this being done by means of steam and water trunnions connecting with the double bottom of each pan. From five to eight pans are supplied in a "battery," although it is often convenient to have one or more pans separately mounted, and without steam taps. The agitation of the contents is performed either by means of wooden paddles or, preferably, by mechanical agitation, which can be raised clear above the top of the pan, and without interfering with the working of the others. As the majority of colors used are made with either starch or flour for thickening, it is necessary, to insure good results, that they are strained or filtered; for this purpose it is well to have wooden frames made, over which is tacked brass or copper wire cloth (iron is inadmissible). The most important piece of apparatus is the printing-machine, an idea of the construction and operation of which may be had from Fig. 125. *A* is a cylindrical "bowl" or drum, covered with several thicknesses of felt cloth, *c*, around this drum, and passing over a smaller one, *B*, is an endless band, *d* (full width of the machine), over this band, and acting as a guide to the fabric to be printed, is another band, *e*, which serves to keep *d* clean, being, in fact, a piece of cloth, yet to be bleached and printed; the piece being printed is indicated by *f*. The means for applying the color are shown in the figure below the large drum,—viz., the printing rollers or engraved cylinders $h_1$, $h_2$, $h_3$, which are fed with color through coming in contact with the wooden rollers $n_1$, $n_2$, $n_3$, which dip in the color contained in the troughs $k_1$, $k_2$, $k_3$. Pressing against each of the rollers, *h*, is shown a small strip of metal, *r*, technically termed the "doctor," the purpose of which is to remove the excess of color from the face of the printing-rollers before they come in contact with the cloth. These "doctors" are best made of bronze or gun-metal, or some of the newer aluminum-copper alloys,—capable of better resisting weak acid. Before the cloth is printed upon it passes over

Fig. 125.

a "lint doctor," the office of which is to remove any loose hair or fibres from the cloth. Printing-machines are built with any number of color boxes and rollers up to twelve or fourteen, each being for a separate color. Sansone mentions one for use with twenty colors. Great nicety is required in adjusting the machines in working to have no overlapping of colors or mordants,—perfect "registration" being sought.

For drying the printed goods revolving cylinders, or "cans" of large diameter, are used, or the goods are passed over heated plates, in no case allowing the printed face to come in contact with any part of the apparatus. Steaming follows to fix the colors. The apparatus being a steamer, as shown on p. 488, or one constructed of brick and iron, acting continuously, thereby turning out much more work than the former. The dyeing- and washing-machines are similar to those already described.

*Mordants, Resists, Discharges, etc.*—All the various substances used in printing must be applied in the form of pastes, the consistency of which must be such that whenever applied they will not run or spread, which impairs the sharpness of outline of the printed pattern. For the purpose the color-mixer has recourse to the starches and gums, the most important of which are *corn*, *wheat starch*, and *flour*, usually made up into ten per cent. pastes. The gums include *gum arabic*, *dextrine* (*British gum*), and *tragacanth*. The first is used in several degrees of consistency, from a fifty to a one hundred and fifty per cent. solution, dextrine the same, and the last in a ten per cent. paste. The proportions are by no means uniform, but they represent the average strengths used in the color house. *Blood albumen* is considerably used, large quantities being manufactured cheaply in Chicago and other Western localities. The mordants used embrace the acetates of alumina of various strengths, basic sulphate, and others of less importance. The acetates and nitrates of iron are the most prominent salts of this element, and of chromium there may be mentioned the acetates and nitrates; others, including salts of tin, calcium, manganese, are also used. Owing to the great number of recipes published for preparing mordants, and of the difficulty in selecting those which may be called representative, only a few will be given of the more important.

*Acetate of Alumina*, or "Red Liquor" (Crookes).—

| | | |
|---|---|---|
| Water | 45 gallons. | 45 gallons. |
| Alum | 100 pounds. | 200 pounds. |
| Acetate of lead | 100 " | 200 " |
| Soda crystals | 10 " | 10 " |

Or the same result can be had by substituting acetate of calcium for the lead salt. In either case the alumina salt is dissolved in about half the quantity of water, and the acetate in the remainder, when the two solutions are mixed and allowed to settle, the precipitated lime or lead sulphate being removed. The addition of soda is to neutralize any free acetic acid.

*Acetate of Iron*, or "Black Iron Liquor," can be obtained either by double decomposition as above, or by dissolving scrap-iron or precipitated oxide of iron in crude acetic acid. In the former method sulphate of iron and acetate of lead are used as follows: Water, forty pounds, sulphate of iron, twenty-four pounds, acetate of lead, twenty-four pounds. Dissolve each separately, mix, and filter. The oxide of iron above mentioned is obtained by precipitating a solution of copperas with ammonia or soda, filtering and washing, and dissolving the moist precipitate in ordinary acetic

acid to make a twenty-five per cent. solution. In the event of using soda, much longer washing is required.

*Nitrate of Iron* is made as above; copperas and nitrate of lead being used for the decompositions in equal proportions. Nitrates made by direct solution are obtained by several methods, the best being nitric acid nearly saturated with scrap-iron and diluted to about 80° Tw. Some of the so-called nitrates of iron are mixtures of sulphate and nitrate of iron and some are composed entirely of sulphate of iron, while others are waste liquors, such as are obtained by dissolving iron out of "tin scrap" by means of sulphuric acid. Others may contain hydrochloric acid, with or without the addition of copperas. *Chromium Acetate* is similarly prepared with chrome alum and lead acetate, or by precipitating chrome alum with an alkali, and dissolving the washed precipitate in acetic acid, or in nitric acid if the nitrate is wanted. This latter mordant can be made by using lead nitrate and chrome alum.

The tin mordants are used to brighten the color with madder and cochineal dyeing. The first is *Stannous Chloride*, $SnCl_2 + 2H_2O$. It is made by dissolving tin in hydrochloric acid and evaporating the solution. It is used somewhat in wool-dyeing, but more largely in calico-printing. Stannic chloride, $SnCl_4$. is also used, and its combination with sal ammoniac known as "Pink Salt," and *Sodium Zincate*, $Na_2SnO_3$, known as "Preparing Salt."

The principal styles of printing tissues are given in the following scheme, condensed from a tabular view given in Sansone's excellent work on "Cotton-Printing."

PRINTED (DIRECT) COLORS.

1. *Steam or Extract Styles.*
   (*a*) *Coal-tar Colors.*
   *Alizarin, Basic Aniline Colors, Acid Colors, and Neutral Azo Colors.*
   (*b*) *Dyewood Extracts* (natural organic coloring matters).
   *Logwood, Quercitron Bark, Sapan and other Red Woods, Catechu, Annatto, Cochineal.*
   (*c*) *Steam Mineral Colors.*
2. *Pigment Styles* (fixed by albumen).
3. *Oxidation Colors.*
4. *Direct Indigo-printing* (alkaline styles).

DYED COLORS.

5. *Alizarin Dyed Styles.*
6. *Turkey-red Styles.*
7. *Indigo Styles.*
8. *Manganese Bronze Styles.*

1. *Steam Styles.*—Here the colors and proper mordants are mixed, and applied to the fabric in one operation, followed by air drying and steaming, or by immediate steaming, drying, and again steaming, the object in each case being to fix and develop the colors. Several conditions are to be noted in this style, chiefly the humidity of the steam, temperature, pressure, and the duration of the steaming, in order that the same shades may be again obtained with the same colors. Before being printed the cloth is passed through a solution of stannate of soda, also called "preparing salt," and then through sulphuric acid (1.005 to 1.015 specific gravity), washed, and dried. The colors best suited are the basic,—that is, those which form insoluble lakes with tannin in combination with a metal, and the general

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method of applying the same is given in the following extract from Sansone ("Printing"), p. 208: "A color is formed consisting of thickening, the solution of coloring matter, and acetic acid. The acetic acid is added in the preparation of the color in order to prevent the tannic acid from combining with the dyestuff; in other words, the acetic acid keeps both the coloring matter and the tannin in solution in the thickened color, and prevents their combining with each other; but when the color is printed and the cloth is dried and steamed, the acetic acid is expelled, and the coloring matter and the tannin then go into combination to form the insoluble colored lake. This lake, however, not being sufficiently fast to stand by itself, a metallic mordant is necessary to give additional fastness to the colors; for this reason the cloth, after printing, dyeing, and steaming, is passed into a solution containing tartar emetic." The antimony of which at once unites with the "tannate" of the color already on the fabric, thereby producing a more insoluble body. The steaming operation must be conducted with such a volume of steam that the acetic acid volatilized can be carried away, or else the colors may be injured. Of the colors employed may be mentioned the Fuchsines, Methyl Violets and Greens, Bismarck Brown, Naphthylene Blue, etc.

*Alizarin*, without exception, is the most important coloring matter used in cotton-printing, for which purpose the goods are previously treated with alizarin oil and dried. With alizarin in printing, as in dyeing, the color obtained depends upon the selection of the mordant, which can, however, be a mixture; for *reds*, alumina, with or without tin; *purples*, iron; *browns*, with either ferricyanide of potassium or acetate of iron, and acetate of alumina, or with chromium mordants. When the fabrics have been printed they are steamed for one or two hours, and passed through a heated chalk-bath, washed, and soaped. The following indicate the methods of preparing several colors:

*Red.* (Standard.)

| | |
|---|---|
| Alizarin paste (fifteen per cent.) | 6 pounds. |
| Starch paste | 2 gallons. |
| Acetate of alumina (11° Bé.) | 1¼ pints. |
| Acetate of lime (15° Bé.) | 1 pint. |
| Nitrate of alumina (13° Bé.) | ¾ " |

*Purple.* (Standard.)

| | |
|---|---|
| Alizarin | 2 pounds. |
| Starch paste | 1 gallon. |
| Acetate of iron (13° Bé.) | 1 quart. |
| Acetate of lime (13° Bé.) | 1 pint. |
| Acetic acid | 1 " |

*Brown.* (Standard.)

| | |
|---|---|
| Alizarin (fifteen per cent.) | 4 pounds. |
| Starch paste | 1 gallon. |
| Nitro-acetate of chromium (25° Bé.) | 3 pounds. |
| Acetate of lime (13° Bé.) | ¼ pound. |

Since the introduction of the alizarin greens and violets, their use in connection with chromium in cotton-printing has been most rapid.

*Dye-woods*, with the exception of logwood, have been nearly superseded by the tar colors. The method of applying the color is nearly the same as for other steam colors,—viz., print, dry in the air, steam, and wash, and is made up with chromium as the mordant, and an oxidizing agent, with or without the presence of another coloring matter to modify the shade.

The following recipes illustrate the color as made for blacks:

*Steam Logwood Black.* (Sansone.)

| | | |
|---|---|---|
| Water | 1 | gallon. |
| Acetic acid (6° Tw.) | 1 | " |
| Logwood extract (30° Tw.) | 1 | " |
| Quercitron bark extract (30° Tw.) | 2 | pounds. |
| Starch | 5 | " |
| Dextrine | 2.5 | " |
| Olive oil | .5 | " |
| Chlorate of potash or soda | .75 | pound. |
| Boil, stir, until cold, then add | | |
| Acetate of chromium (20° Tw.) | 1 | gallon. |

*Steam Logwood Black.* (Sansone.)

| | | |
|---|---|---|
| Starch | 6 | pounds. |
| Flour | 6 | " |
| Acetic acid (6° Tw.) | 2.5 | gallons. |
| Logwood extract (20° Tw.) | 3.5 | " |
| Acetate of iron (15° Tw.) | 3.5 | " |
| Olive oil | 1.5 | pounds. |

Of the other natural coloring matters there may be mentioned *Cochineal*, applied with *tin* or *alumina; Sapan*, in the same manner, and *Quercitron Bark*, with *alumina* or *chromium*. *Catechu*, much used for *browns*, may be applied with acetate of chromium or with logwood and fuchsine.

The *Mineral Colors* are to some extent made use of, their application depending upon the principle of double decomposition upon its fibre when subjected to steaming. The following examples will make the principle clear: Yellows are obtained by the decomposition of nitrate of lead and a soluble chromate, the insoluble *chromate of lead* ("chrome yellow") being formed. For Blues, both prussiates of potash are used. Brown is obtained by means of chloride of manganese and bichromate of potash.

2. *Pigment Styles.*—For this style effects are produced by means of insoluble color lakes and the mineral colors, which are fixed upon the cloth by steaming, the action of which coagulates the albumen with which the colors are invariably mixed for printing. The colors are generally supplied to the color-mixer in a dry condition, and include *Ultramarine* of various qualities, *Vermilion* (sulphide of mercury), the *Chromates of Lead and Barium*, *Cadmium Yellow* (cadmium sulphide), *Chrome Green* (oxide of chromium), the *Ochres*, yellow and red, and *Lamp-black*. A familiar example of this style is seen in cheap flags and decorative muslins.

3. *Oxidation Colors.*—The most important of this class is *Aniline Black*, and will be briefly outlined as follows: Aniline oil is made into a paste with a chlorate (soda generally) and a metallic salt, with the proper amount of starch paste. This is printed upon the fabric, "aged" for forty-eight hours, or passed through a "steam ager," then passed through a warm bath of bichromate of potash, washed well, and finally worked through a soap-bath. The metallic salt mentioned acts as a carrier of oxygen, and for the purpose vanadate of ammonium, sulphide of copper, bichromate of potash, etc., are used. For the preparation of the color paste the following methods are given:

| | | |
|---|---|---|
| 1. Water | 1 | gallon. |
| Aniline salt | 2 | pounds. |
| Aniline oil | 2 | " |
| Starch | 2 | " |
| Dextrine | ½ | pound. |

The paste is made first with the starch and dextrine, then the aniline is added.

| | |
|---|---|
| 2. Chlorate of soda (8° Bé.) | 1 gallon. |
| Starch | 2 pounds. |
| Dextrine | ½ pound. |
| Chloride of ammonium | ½ " |

These are made separately, but when wanted are mixed, and two pounds of *sulphide of copper* paste are added, and the whole well mixed and strained. (Crookes.)

The use of vanadium is shown by the following method (Sansone, "Printing," p. 275):

| | |
|---|---|
| Water | 1 gallon. |
| Starch | 1½ pounds. |
| Dextrine | ¾ " |
| Boil, cool down to 120° F., then add | |
| Aniline oil | 1½ " |
| previously neutralized with | |
| Hydrochloric acid (32° Tw.) | 1½ " |
| Stir until cold, then add a cold solution of | |
| Chlorate of soda | ¾ pound. |
| Boiling water | 1 " |
| Before printing add further | |
| Vanadium solution | ½ " |

Print, dry not too hard, age two days, then pass through two per cent. solution of bichromate of potash at 160° F., wash and soap.

The vanadium solution is made with vanadate of ammonia, hydrochloric acid, glycerine, and water, and contains about .15 gramme per litre.

Other colors are produced by oxidation,—namely, Brown (with phenylen diamine, Sansone), by simply printing with a chlorate, drying, and steaming, Yellow, Grays, Olives, Blues, etc. To obtain white patterns on goods printed with aniline black, a "*resist*" or "*reserve*" is first applied of the desired pattern, consisting of white arsenic as the base, with caustic soda, and the proper thickening. For *discharging* the aniline black after it is printed, permanganate of potash is used; the goods are afterwards passed through a solution of oxalic acid.

4. *Indigo-printing.*—Indigo is printed upon cotton fabrics in two ways, one of which is known as the "Glucose," and the other the "Reduced Indigo" Process. The former is carried out as follows: Indigo is finely ground, and made into a paste with water, to which is added caustic soda; this is now kept in a closed vessel in order to prevent as much as possible the absorption of carbonic oxide from the atmosphere. When used in printing, it is thickened with dextrine and starch; the following table (from Sansone, "Cotton-Printing," p. 284) showing the proportions used for several shades:

| | Dark blue. | Medium blue. | Light blue. |
|---|---|---|---|
| Light calcined starch | 3 parts. | 3 parts. | 3 parts. |
| Indian corn starch | 1½ " | 1½ " | 1½ " |
| Water | 3¾ " | 3¾ " | 3¾ " |
| Caustic soda lye (70° Tw.) | 16 " | 28 " | 40 " |
| Indigo paste | 30 " | 18 " | 6 " |

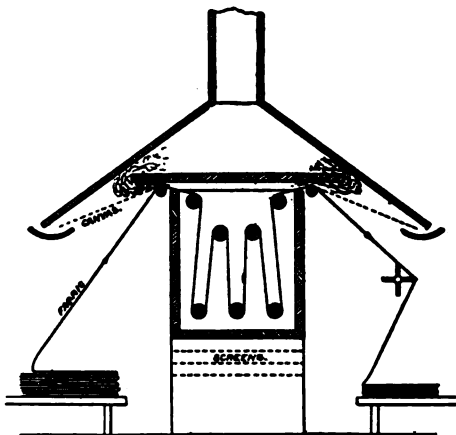
The cloth, before being printed upon, is worked through a twenty-five per cent. solution of glucose and dried. After printing, the cloth must be again dried and passed through an atmosphere of wet steam, in an apparatus shown in Fig. 126, to effect the reduction of the indigo which now takes place. The cloth is now washed in water, being repeatedly, during the washing, exposed to the air, when the *reduced* indigo is oxidized and its real color appears. The reason for rapidly steaming is to act upon the

caustic alkali while it is still in that state, as if it should become carbonated through delay little reduction will take place. This method is employed in printing indigo upon alizarin-dyed goods and in other combinations with resists, etc.

The "*Reduced Indigo Process*" is based upon the fact that indigo, when finely ground and mixed with lime and thiosulphate of soda in suitable thickening agents, is reduced; if, with this reduced indigo paste, patterns are printed upon cotton fabrics, and then exposed to the air, the indigo is oxidized with a regeneration of the blue color. The pieces are then washed and dried.

FIG. 126.

Instead of using indigo in printing, one of the newer colors, *Immedial Blue*, is now very extensively used and printed with suitable mordants directly upon the goods.

5. *Dyed Alizarin.*—This process differs from all those previously mentioned in that the colors are produced by first *printing* upon the fabric the thickened mordants suited to alizarin, *ageing*, during which the mordants so printed are decomposed and more firmly fixed upon the cloth, *dunging*, an operation which removes the thickening no longer needed, followed by a washing, and then *dyeing* with alizarin, and, finally, *brightening*. The mordants used for Reds are generally made with acetate of alumina, thickened with starch or flour, and dextrine, while by the addition of tin to such a mixture blue shades will be obtained. For Purples or Violets, acetate of iron is used diluted with paste, if used strong, blacks can be produced. Browns are obtained with catechu and copper acetates. Mixtures of the acetates of iron and alumina yield varying shades of Chocolate. Following the printing operation, the fabric is allowed to dry, when it is aged by being caused to pass through the continuous steamer; here the acetates are decomposed, basic salts remaining fixed upon the cloth. Formerly the operation was conducted in large rooms, and often required a week to finish; now long chambers provided with a series of rollers, and with requisite means for steam control, are used; it must be remarked that colors obtained upon cloth rapidly aged do not compare in fastness with those obtained upon cloth slowly aged. Dunging is merely a transmission of the aged cloth through solutions of phosphate, arseniate, or silicate of soda, these chemicals having displaced the somewhat offensive cow-dung in the operations of precipitating the mordant upon the fibre, and also to remove the thickening and excess of mordant, after which the cloth is well washed and then dyed. The dye-bath is made up with alizarin, alizarin oil, tannin, etc., in a similar manner to that described under Dyeing (p. 487), after which the cloth washed, worked in alizarin oil, dried, and steamed, then washed and soaped. In case reds have been dyed, and it is desirable to reduce their tone, "*cutting*" is resorted to after the soaping, by means of a solution of stannic chloride.

*Resists* are substances printed upon the fabric which will prevent the fixation of color at those places, and are of two kinds, chemical and mechanical; the former are composed chiefly of citric acid, while the latter are made up of some inert substances, such as pipe-clay, beeswax, etc. Thus a resist (or reserve) of citrate of soda (lime-juice and soda lye) when applied to the cloth prevents the fixation of the oxides of iron or alumina on the fibre, and therefore when the cloth is afterwards dunged and dyed in the alizarin bath the reserved spots remain white, while the colors will be formed where the mordant has been fixed. In this way not only reds and pinks can be reserved, but purples, chocolates, and blacks also. *Discharges* are substances printed upon goods the whole of which had been mordanted, the object being to remove the mordant from places where whites are to appear, consequently when the piece is dyed only where the mordant is intact will the cloth be colored; these discharges are made principally with citric, tartaric, or acetic acid. This acid-containing discharge having been printed on, the goods are then taken through a solution of bleaching-powder (chloride of lime). The result is that when the acids have been printed on chlorine gas is liberated, which destroys the dye-color, leaving in the simplest cases a white design upon a colored ground.

6. *Turkey-red Styles.*—This process is simply printing upon cloth which has previously been dyed Turkey-red (see p. 487) by means of discharges, which may or may not be made so as to yield colored patterns. The base is citric or tartaric acid, thickened with a suitable paste, and if for colors, containing a salt of lead, if for a yellow discharge, or ferro-prussiate of potash, for a blue discharge, or iron and logwood, for a black discharge. After printing on the discharges, the goods are passed through a bath of bleaching-powder, well washed, and then, if lead has been printed on, passed through a bath of bichromate of potash, when chrome yellow will be produced. If the prussiate of potash has been printed, a blue color will be developed. Green is obtained by mixing both discharges first.

7. *Indigo Styles* are similar to the above; resists are printed on the cloth, which is then dyed in the vat in the ordinary manner, when, upon a removal of the resist by suitable means, white patterns are had upon a blue ground. By the system of discharges various colors may be put on by means of lead and other metallic salts. Vermilion is applied directly with albumen. For a discharge which has to be afterwards dyed red with alizarin, bromide of manganese and an aluminum salt are used.

8. *Manganese Bronze Style*, or *Bistre Style.*—This process has for its object the production of hydrated peroxide of manganese upon the fibre, and the subsequent printing of colors by means of discharges. The goods are worked in a solution of manganous chloride, dried, and worked in soda lye, washed, and passed through a solution of chloride of lime until a brown color is produced. Wash, dry, and the goods are ready for printing. A discharge for white is made with muriate of tin (120° Tw.); for blue, yellow prussiate of potash with an organic acid; for yellow, a lead salt, developed with bichromate of potash. Green and black as in the previous style.

*Woollen- and Silk-printing.*—*Wool*, either as yarn or fabric, is generally printed with the tar colors, and according to the steam style previously described. The goods are dried after printing, steamed for one hour, and well washed. *Silk* is printed in the same style after being prepared by suitable agents, such as tin with or without an acid. Previous to being printed both silk and wool must be entirely free from grease.

The following table from Rupe's "Chemie der Natürlichen Farbstoffe" (Braunschweig, 1900) shows the artificial dye-colors which have replaced or are in practical use competing with the natural dyestuffs named:

| NATURAL DYESTUFFS. | Is displaced for cotton. | Is displaced for wool and silk. |
|---|---|---|
| QUERCITRON . . . . . | Mainly by substantive dye-colors: *Diamine fast yellow B A* (C.), *Chloramine yellow* (C.), *Chrysophenine* (C.), *Auramine* (H. G.), *Diamine yellow* (H.), *Chrysamine* (H.), *Thioflavine* (G.). For printing along with logwood it is still used as before. | Is not much used now, the different mordant coloring yellows having taken its place. In addition, *Naphthol yellow S* (H.), *Tartrazine*, *Quinoline yellow* (H.). |
| PERSIAN BERRIES . . | Are still much used in cotton-printing and in connection with tin salts. For direct printing compete: *Auramine*, *Thioflavine T* (C.), the latter exclusively for discharges; in addition, *Chrysophenine* (H.), *Chloramine yellow* (H.), *Oriol* (G.). Important are also the yellow salicylic acid azo colors, such as *Alizarin yellow* (H.), etc. | Little used for wool. For silk replaced by *Tartrazine*, *Fulling yellow* (C.), *Naphthol yellow S* (H.). |
| WELD . . . . . . . . | Is hardly ever used for cotton. | Is little used for wool, but, on the other hand, largely for silk. Is replaced by *Naphthol yellow S*, *Fast yellow* (C.), *Tartrazine*, *Fulling yellow* (C.), *Citronine* (G.), *Jasmine* (G.), *Azo yellow* (G.), *Alizarin yellow* (H.). |
| FUSTIC . . . . . . . . | Almost entirely displaced by the substantive yellow dyes, as with quercitron. In addition, *Sun yellow* (G.), *Diphenyl fast yellow* (G.), *Cresotin yellow* (G.), also by *Alizarin yellow* and its homologues (H.). For printing in connection with logwood it is still unreplaced. | Is still much used in wool-dyeing, although strongly pushed by the different mordant-attracting yellows: *Anthracene yellow C* (C. G.), *Chrome yellow* (C. G.), *Mordant yellow* (C. G.), *Fulling yellow* (C.), *Azo yellow* (H.), *Fast yellow* (H.), *Alizarin yellow* (H.). |
| LOGWOOD . . . . . . | In cotton dyeing (for black) is about given up. For better goods is replaced by *Aniline black*, *Diaminogen black* (C.), for cheaper goods by the direct dyeing and diazotizable blacks: *Diamine black* (C.), *Oxydiamine black* (C.), *Columbia black* (C.), *Direct deep black* (C.), also by *Vidal black*, *Immedial black* (G. H.), and similar sulphated products. | With wool the case is the same as with cotton. It is still used for dyeing, but is losing ground rapidly. The substitutes are: *Naphthol* and *Naphthylamine black* (C. G. H.), *Brilliant black* (C. G.), *Diamond black* (C. G. H.), *Wool black* (C.), *Alizarin black* (G. H.), *Anthracene black* (C. G.), *Azo acid black* (H.), *Chromotrope S* (H.). For silk, still used enormously and with no substitute. |
| BRAZIL-WOOD . . . . | For cotton scarcely used now, being replaced by the substantive dyeing reds: *Diamine fast red F* (C.), *Congorubine* (C.), *Diamine bordeaux* (C.), *Benzopurpurine* (G. H.), *Diamine red* (H.), also by *Fuchsine* (G. H.), *Hessian purple* (G.), *Safranine*, (H.), *Paranitraniline red* (H.), *Alizarin red* (H.). | Also for wool and silk almost entirely replaced by *Cloth red* (C.), *Wool red* (C.), *Acid fuchsine* (G.), *Fast red* (H.), *Archil substitute* (G.), *Ponceau* (H.), *Apollo red* (G.), *Rocellin* (G.); in the fulling industry by *Alizarin red* (C. H.), *Diamine fast red* (C.), *Chromotrope* (H.). |
| COCHINEAL . . . . . | . . . . . . . . . . . . . . . . . . . . | Is still used somewhat for wool and silk, but is being displaced by vivid acid wool colors, such as *Azoeosin* (G.), *Chromazon red* (G.), *Palatine scarlet* (H. C.), *Brilliant croceïn* (H.), *Brilliant cochineal* (C.), and the different *Ponceaux*, etc. |
| ARCHIL . . . . . . . | . . . . . . . . . . . . . . . . . . . . | Has practically been entirely displaced for wool and silk by the readily levelling red acid wool dyes: *Acid fuchsine* (C.), *Azocarmine* (C. G. H.), *Archil substitute* (C. G. H.), *Azofuchsine* (C. G. H.), *Lanafuchsine* (C.), *Azorubine* (C.), *Azo acid fuchsine* (H.), *Rosinduline* (G.), *Apollo red* (G.), *Chromotrope* (H.). |
| ANNATTO . . . . . . | For cotton is replaced by the different artificial orange colors, as *Chrysophenine* (H.), *Chrysamine* (H.), *Mikado yellow* and *orange* (H.). | . . . . . . . . . . . . . . . . . . . . |

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| Natural Dyestuffs. | Is displaced for cotton. | Is displaced for wool and silk. |
|---|---|---|
| Safflower | Was first replaced for cotton by the *Eosines*, *Phloxine* (C. G.); later these were displaced by *Rhodamine* (C. G.), *Erica* (C.), *Diamine rose* (C.), *Geranine* (C.), *Safranine* (H.), etc. | . . . . . . . . . . |
| Berberine | . . . . . . . . . . | Is not used for wool, but still somewhat for silk. Substitutes are the same as those mentioned for Weld. |
| Catechu | Still used for cotton, although a whole series of excellent substantive dyes have appeared. Especially have the *Diamine* colors, *Benzo* and *Congo* colors with supplementary treatment with chrome and copper, recently competed successfully (C.), and *Chrysoidine* (H.), *Vesuvine* (H.), etc. For calico-printing, catechu is still very largely used, although the different *Alizarin* colors are seeking to displace it in part (C.). | Still used for silk in combination with logwood in large amount without any competing products (C.). For weighting of silk. |
| Indigo | Despite the many seriously competing products is still much used for cotton. These competing products are: *Synthetic indigo*, *Indoin* (C. G. H.), *Naphthindon* (C.), *Fast cotton blue* (C.), *Methylene blue* (C. H.), *Indamine blue* (H.), *Janus blue* (H.), and the direct coloring and diazotizable blues of the Diamine, Diphenyl, and Benzo color groups. [*Diamine blue* and related colors (H.), *Diaminogen blue* (C. H.).] A new product, *Immedial blue* (C. H.), belonging to the sulphated colors, which has recently appeared, seems to be among the most important substitutes. In calico-printing, Indigo has been in part replaced by the *Synthetic indigo* preparations and by the different basic blues, including *Nitroso blue*, *Alizarin blue*, etc. (C.). | On wool, is replaced on the one hand by *Alizarin blue* (C. G. H.), *Synthetic indigo*, *Alizarin cyanine* (C. G. H.), *Anthracene blue* (G. H.), *Chromotrope F B* (H.), *Gallamine blue* (G.), *Gallocyanine* (G.), and on the other hand by *Sulphocyanine* (C.) and *Lanacyl blue*. However, the application of Indigo to wool still holds out relatively well. |

The communications upon which this table is based were from the firms of Leopold Casella & Co., of Frankfurt-am-Main (C.), Joh. Rud. Geigy & Co., of Basel (G.), and Farbwerke, vormals Meister, Lucius and Brüning, of Höchst (H.).

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# APPENDIX.

## I. The Metric System.

THE French *metric* system is based upon the idea of employing, as the unit of all measures, whether of length, capacity, or weight, a uniform unchangeable standard, adopted from nature, the multiples and subdivisions of which should follow in decimal progression. To obtain such a standard, the length of one-fourth part of the terrestrial meridian, extending from the equator to the pole, was ascertained. The ten-millionth part of this arc was chosen as the unit of measures of length, and was denominated *metre*. The cube of the tenth part of the metre was taken as the unit of measures of capacity, and denominated *litre*. The weight of distilled water, at its greatest density, which this cube is capable of containing, was called *kilogramme*, of which the thousandth part was adopted as the unit of weight, under the name of *gramme*. The multiples of these measures, proceeding in a decimal progression, are distinguished by employing the prefixes, *deca*, *hecto*, *kilo*, and *myria*, taken from the Greek numerals; and the subdivisions, following the same order, by *deci*, *centi*, *milli*, from the Latin numerals. Since the introduction of this system it has been adopted by the principal nations of Europe, excepting Great Britain, and in many of them its use is compulsory. It is in general use in France, Germany, Austria, Italy, Spain, Norway, Sweden, Netherlands, Switzerland, Greece, and British India. It was legalized in Great Britain in 1864, and in the United States by an act of Congress in 1866.

| | | |
|---|---|---|
| The *metre*, or unit of length, at 32°, | = | 39.370432 inches. |
| The *litre*, or unit of capacity, | = | 33.816 fluidounces. *U. S.* |
| The *gramme*, or unit of weight, | = | 15.43234874 Troy grains. |

Upon this basis the following tables have been constructed:

MEASURES OF LENGTH.

| | | English inches. | | | English inches. |
|---|---|---|---|---|---|
| Millimetre (mm.) | = | .03937 | Decametre (Dm.) | = | 393.70432 |
| Centimetre (cm.) | = | .39370 | Hectometre (Hm.) | = | 3937.04320 |
| Decimetre (dm.) | = | 3.93704 | Kilometre (Km.) | = | 39370.43200 |
| Metre (m.) | = | 39.37043 | Myriametre (Mm.) | = | 393704.32000 |

MEASURES OF CAPACITY.

| | | English cubic inches. | | | English cubic inches. |
|---|---|---|---|---|---|
| Millilitre (ml.) | = | .061028 | Decalitre (Dl.) | = | 610.280000 |
| Centilitre (cl.) | = | .610280 | Hectolitre (Hl.) | = | 6102.800000 |
| Decilitre (dl.) | = | 6.102800 | Kilolitre (Kl.) | = | 61028.000000 |
| Litre (l.) | = | 61.028000 | Myrialitre (Ml.) | = | 610280.000000 |

MEASURES OF WEIGHT.

| | | Troy grains. | | | Troy grains. |
|---|---|---|---|---|---|
| Milligramme (mg.) | = | .0154 | Decagramme (Dg.) | = | 154.3234 |
| Centigramme (cg.) | = | .1543 | Hectogramme (Hg.) | = | 1543.2348 |
| Decigramme (dg.) | = | 1.5432 | Kilogramme (Kg.) | = | 15432.3487 |
| Gramme (gm.) | = | 15.4323 | Myriagramme (Mg.) | = | 154323.4874 |

*Value of Avoirdupois Weights and Imperial Measures, in Metric Weights and Measures, as stated in the British Pharmacopœia.*

| Avoirdupois weights. | | Metric weights. | Imperial measures. | | Metric measures. |
|---|---|---|---|---|---|
| 1 pound | = | 453.5925 grammes. | 1 gallon | = | 4.543487 litres. |
| 1 ounce | = | 28.3495 " | 1 pint | = | 0.567936 " |
| 1 grain | = | 0.0648 " | 1 fluidounce | = | 0.028396 " |
| | | | 1 fluidrachm | = | 0.003549 " |
| | | | 1 minim | = | 0.000059 " |

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## II. Tables for Determination of Temperature.

### RELATIONS BETWEEN THERMOMETERS.

In *Fahrenheit's* thermometer, the freezing-point of water is placed at 32°, and the boiling-point at 212°, and the number of intervening degrees is 180.

The *Centigrade* or *Celsius's* thermometer, which is now recognized in the U. S. Pharmacopœia and has been adopted generally by scientists, marks the freezing-point *zero*, and the boiling-point 100°.

From the above statement, it is evident that 180 degrees of Fahrenheit are equal to 100° of the Centigrade, or one degree of the first is equal to $\frac{5}{9}$ of a degree of the second. It is easy, therefore, to convert the degrees of one into the equivalent number of degrees of the other; but in ascertaining the corresponding points upon the different scales, it is necessary to take into consideration their different modes of graduation. Thus, as the zero of Fahrenheit is 32° below the point at which that of the Centigrade is placed, this number must be taken into account in the calculation.

1. If any degree on the *Centigrade* scale, either above or below zero, be multiplied by 1.8, the result will, in either case, be the number of degrees above or below 32°, or the freezing-point of *Fahrenheit*.

2. The number of degrees between any point of *Fahrenheit's* scale and 32°, if divided by 1.8, will give the corresponding point on the *Centigrade*.

## THERMOMETRIC EQUIVALENTS.

According to the Centigrade and Fahrenheit Scales.

| C.° | F.° | C.° | F.° | C.° | F.° | C.° | F.° | C.° | F°. |
|---|---|---|---|---|---|---|---|---|---|
| —39.4 | —39 | —17.2 | 1 | 5 | 41 | 27.2 | 81 | 49.4 | 121 |
| —39 | —38.2 | —17 | 1.4 | 5.5 | 42 | 27.7 | 82 | 50 | 122 |
| —38.8 | —38 | —16.6 | 2 | 6 | 42.8 | 28 | 82.4 | 50.5 | 123 |
| —38.3 | —37 | —16.1 | 3 | 6.1 | 43 | 28.3 | 83 | 51 | 123.8 |
| —38 | —36.4 | —16 | 3.2 | 6.6 | 44 | 28.8 | 84 | 51.1 | 124 |
| —37.7 | —36 | —15.5 | 4 | 7 | 44.6 | 29 | 84.2 | 51.6 | 125 |
| —37.2 | —35 | —15 | 5 | 7.2 | 45 | 29.4 | 85 | 52 | 125.6 |
| —37 | —34.6 | —14.4 | 6 | 7.7 | 46 | 30 | 86 | 52.2 | 126 |
| —36.6 | —34 | —14 | 6.8 | 8 | 46.4 | 30.5 | 87 | 52.7 | 127 |
| —36.1 | —33 | —13.8 | 7 | 8.3 | 47 | 31. | 87.8 | 53 | 127.4 |
| —36 | —32.8 | —13.3 | 8 | 8.8 | 48 | 31.1 | 88 | 53.3 | 128 |
| —35.5 | —32 | —13 | 8.6 | 9. | 48.2 | 31.6 | 89 | 53.8 | 129 |
| —35 | —31 | —12.7 | 9 | 9.4 | 49 | 32 | 89.6 | 54 | 129.2 |
| —34.4 | —30 | —12.2 | 10 | 10 | 50 | 32.2 | 90 | 54.4 | 130 |
| —34 | —29.2 | —12 | 10.4 | 10.5 | 51 | 32.7 | 91 | 55 | 131 |
| —33.8 | —29 | —11.6 | 11 | 11 | 51.8 | 33 | 91.4 | 55.5 | 132 |
| —33.3 | —28 | —11.1 | 12 | 11.1 | 52 | 33.3 | 92 | 56 | 132.8 |
| —33 | —27.4 | —11 | 12.2 | 11.6 | 53 | 33.8 | 93 | 56.1 | 133 |
| —32.7 | —27 | —10.5 | 13 | 12 | 53.6 | 34 | 93.2 | 56.6 | 134 |
| —32.2 | —26 | —10 | 14 | 12.2 | 54 | 34.4 | 94 | 57 | 134.6 |
| —32 | —25.6 | —9.4 | 15 | 12.7 | 55 | 35 | 95 | 57.2 | 135 |
| —31.6 | —25 | —9 | 15.8 | 13 | 55.4 | 35.5 | 96 | 57.7 | 136 |
| —31.1 | —24 | —8.8 | 16 | 13.3 | 56 | 36 | 96.8 | 58 | 136.4 |
| —31 | —23.8 | —8.3 | 17 | 13.8 | 57 | 36.1 | 97 | 58.3 | 137 |
| —30.5 | —23 | —8 | 17.6 | 14 | 57.2 | 36.6 | 98 | 58.8 | 138 |
| —30 | —22 | —7.7 | 18 | 14.4 | 58 | 37 | 98.6 | 59 | 138.2 |
| —29.4 | —21 | —7.2 | 19 | 15 | 59 | 37.2 | 99 | 59.4 | 139 |
| —29 | —20.2 | —7 | 19.4 | 15.5 | 60 | 37.7 | 100 | 60 | 140 |
| —28.8 | —20 | —6.6 | 20 | 16 | 60.8 | 38 | 100.4 | 60.5 | 141 |
| —28.3 | —19 | —6.1 | 21 | 16.1 | 61 | 38.3 | 101 | 61 | 141.8 |
| —28 | —18.4 | —6 | 21.2 | 16.6 | 62 | 38.8 | 102 | 61.1 | 142 |
| —27.7 | —18 | —5.5 | 22 | 17 | 62.6 | 39 | 102.2 | 61.6 | 143 |
| —27.2 | —17 | —5 | 23 | 17.2 | 63 | 39.4 | 103 | 62 | 143.6 |
| —27 | —16.6 | —4.4 | 24 | 17.7 | 64 | 40 | 104 | 62.2 | 144 |
| —26.6 | —16 | —4 | 24.8 | 18 | 64.4 | 40.5 | 105 | 62.7 | 145 |
| —26.1 | —15 | —3.8 | 25 | 18.3 | 65 | 41 | 105.8 | 63 | 145.4 |
| —26 | —14.8 | —3.3 | 26 | 18.8 | 66 | 41.1 | 106 | 63.3 | 146 |
| —25.5 | —14 | —3 | 26.6 | 19 | 66.2 | 41.6 | 107 | 63.8 | 147 |
| —25 | —13 | —2.7 | 27 | 19.4 | 67 | 42 | 107.6 | 64 | 147.2 |
| —24.4 | —12 | —2.2 | 28 | 20 | 68 | 42.2 | 108 | 64.4 | 148 |
| —24 | —11.2 | —2 | 28.4 | 20.5 | 69 | 42.7 | 109 | 65 | 149 |
| —23.8 | —11 | —1.6 | 29 | 21 | 69.8 | 43 | 109.4 | 65.5 | 150 |
| —23.3 | —10 | —1.1 | 30 | 21.1 | 70 | 43.3 | 110 | 66 | 150.8 |
| —23 | —9.4 | —1 | 30.2 | 21.6 | 71 | 43.8 | 111 | 66.1 | 151 |
| —22.7 | —9 | —0.5 | 31 | 22 | 71.6 | 44 | 111.2 | 66.6 | 152 |
| —22.2 | —8 | 0 | 32 | 22.2 | 72 | 44.4 | 112 | 67 | 152.6 |
| —22 | —7.6 | 0.5 | 33 | 22.7 | 73 | 45 | 113 | 67.2 | 153 |
| —21.6 | —7 | 1 | 33.8 | 23 | 73.4 | 45.5 | 114 | 67.7 | 154 |
| —21.1 | —6 | 1.1 | 34 | 23.3 | 74 | 46 | 114.8 | 68 | 154.4 |
| —21 | —5.8 | 1.6 | 35 | 23.8 | 75 | 46.1 | 115 | 68.3 | 155 |
| —20.5 | —5 | 2 | 35.6 | 24 | 75.2 | 46.6 | 116 | 68.8 | 156 |
| —20 | —4 | 2.2 | 36 | 24.4 | 76 | 47 | 116.6 | 69 | 156.2 |
| —19.4 | —3 | 2.7 | 37 | 25 | 77 | 47.2 | 117 | 69.4 | 157 |
| —19 | —2.2 | 3 | 37.4 | 25.5 | 78 | 47.7 | 118 | 70 | 158 |
| —18.8 | —2 | 3.3 | 38 | 26 | 78.8 | 48 | 118.4 | 70.5 | 159 |
| —18.3 | —1 | 3.8 | 39 | 26.1 | 79 | 48.3 | 119 | 71 | 159.8 |
| —18 | —0.4 | 4. | 39.2 | 26.6 | 80 | 48.8 | 120 | 71.1 | 160 |
| —17.7 | 0 | 4.4 | 40 | 27 | 80.6 | 49 | 120.2 | 71.6 | 161 |

*Thermometric Equivalents.*—Continued.

| C.° | F.° | C.° | F.° | C.° | F.° | C.° | F.° | C.° | F.° |
|---|---|---|---|---|---|---|---|---|---|
| 72 | 161.6 | 95.5 | 204 | 118.8 | 246 | 142.2 | 288 | 166 | 330.8 |
| 72.2 | 162 | 96 | 204.8 | 119 | 246.2 | 142.7 | 289 | 166.1 | 331 |
| 72.7 | 163 | 96.1 | 205 | 119.4 | 247 | 143 | 289.4 | 166.6 | 332 |
| 73 | 163.4 | 96.6 | 206 | 120 | 248 | 143.3 | 290 | 167 | 332.6 |
| 73.3 | 164 | 97 | 206.6 | 120.5 | 249 | 143.8 | 291 | 167.2 | 333 |
| 73.8 | 165 | 97.2 | 207 | 121 | 249.8 | 144 | 291.2 | 167.7 | 334 |
| 74 | 165.2 | 97.7 | 208 | 121.1 | 250 | 144.4 | 292 | 168 | 334.4 |
| 74.4 | 166 | 98 | 208.4 | 121.6 | 251 | 145 | 293 | 168.3 | 335 |
| 75 | 167 | 98.3 | 209 | 122 | 251.6 | 145.5 | 294 | 168.8 | 336 |
| 75.5 | 168 | 98.8 | 210 | 122.2 | 252 | 146 | 294.8 | 169 | 336.2 |
| 76 | 168.8 | 99 | 210.2 | 122.7 | 253 | 146.1 | 295 | 169.4 | 337 |
| 76.1 | 169 | 99.4 | 211 | 123 | 253.4 | 146.6 | 296 | 170 | 338 |
| 76.6 | 170 | 100 | 212 | 123.3 | 254 | 147 | 296.6 | 170.5 | 339 |
| 77 | 170.6 | 100.5 | 213 | 123.8 | 255 | 147.2 | 297 | 171 | 339.8 |
| 77.2 | 171 | 101 | 213.8 | 124 | 255.2 | 147.7 | 298 | 171.1 | 340 |
| 77.7 | 172 | 101.1 | 214 | 124.4 | 256 | 148 | 298.4 | 171.6 | 341 |
| 78 | 172.4 | 101.6 | 215 | 125 | 257 | 148.3 | 299 | 172 | 341.6 |
| 78.3 | 173 | 102 | 215.6 | 125.5 | 258 | 148.8 | 300 | 172.2 | 342 |
| 78.8 | 174 | 102.2 | 216 | 126 | 258.8 | 149 | 300.2 | 172.7 | 343 |
| 79 | 174.2 | 102.7 | 217 | 126.1 | 259 | 149.4 | 301 | 173 | 343.4 |
| 79.4 | 175 | 103 | 217.4 | 126.6 | 260 | 150 | 302 | 173.3 | 344 |
| 80 | 176 | 103.3 | 218 | 127 | 260.6 | 150.5 | 303 | 173.8 | 345 |
| 80.5 | 177 | 103.8 | 219 | 127.2 | 261 | 151 | 303.8 | 174 | 345.2 |
| 81 | 177.8 | 104 | 219.2 | 127.7 | 262 | 151.1 | 304 | 174.4 | 346 |
| 81.1 | 178 | 104.4 | 220 | 128 | 262.4 | 151.6 | 305 | 175 | 347 |
| 81.6 | 179 | 105 | 221 | 128.3 | 263 | 152 | 305.6 | 175.5 | 348 |
| 82 | 179.6 | 105.5 | 222 | 128.8 | 264 | 152.2 | 306 | 176 | 348.8 |
| 82.2 | 180 | 106 | 222.8 | 129 | 264.2 | 152.7 | 307 | 176.1 | 349 |
| 82.7 | 181 | 106.1 | 223 | 129.4 | 265 | 153 | 307.4 | 176.6 | 350 |
| 83 | 181.4 | 106.6 | 224 | 130 | 266 | 153.3 | 308 | 177 | 350.6 |
| 83.3 | 182 | 107 | 224.6 | 130.5 | 267 | 153.8 | 309 | 177.2 | 351 |
| 83.8 | 183 | 107.2 | 225 | 131 | 267.8 | 154 | 309.2 | 177.7 | 352 |
| 84 | 183.2 | 107.7 | 226 | 131.1 | 268 | 154.4 | 310 | 178 | 352.4 |
| 84.4 | 184 | 108 | 226.4 | 131.6 | 269 | 155 | 311 | 178.3 | 353 |
| 85 | 185 | 108.3 | 227 | 132 | 269.6 | 155.5 | 312 | 178.8 | 354 |
| 85.5 | 186 | 108.8 | 228 | 132.2 | 270 | 156 | 312.8 | 179 | 354.2 |
| 86 | 186.8 | 109 | 228.2 | 132.7 | 271 | 156.1 | 313 | 179.4 | 355 |
| 86.1 | 187 | 109.4 | 229 | 133 | 271.4 | 156.6 | 314 | 180 | 356 |
| 86.6 | 188 | 110 | 230 | 133.3 | 272 | 157 | 314.6 | 180.5 | 357 |
| 87 | 188.6 | 110.5 | 231 | 133.8 | 273 | 157.2 | 315 | 181 | 357.8 |
| 87.2 | 189 | 111 | 231.8 | 134 | 273.2 | 157.7 | 316 | 181.1 | 358 |
| 87.7 | 190 | 111.1 | 232 | 134.4 | 274 | 158 | 316.4 | 181.6 | 359 |
| 88 | 190.4 | 111.6 | 233 | 135 | 275 | 158.3 | 317 | 182 | 359.6 |
| 88.3 | 191 | 112 | 233.6 | 135.5 | 276 | 158.8 | 318 | 182.2 | 360 |
| 88.8 | 192 | 112.2 | 234 | 136 | 276.8 | 159 | 318.2 | 182.7 | 361 |
| 89 | 192.2 | 112.7 | 235 | 136.1 | 277 | 159.4 | 319 | 183 | 361.4 |
| 89.4 | 193 | 113 | 235.4 | 136.6 | 278 | 160 | 320 | 183.3 | 362 |
| 90 | 194 | 113.3 | 236 | 137 | 278.6 | 160.5 | 321 | 183.8 | 363 |
| 90.5 | 195 | 113.8 | 237 | 137.2 | 279 | 161 | 321.8 | 184 | 363.2 |
| 91 | 195.8 | 114 | 237.2 | 137.7 | 280 | 161.1 | 322 | 184.4 | 364 |
| 91.1 | 196 | 114.4 | 238 | 138 | 280.4 | 161.6 | 323 | 185 | 365 |
| 91.6 | 197 | 115 | 239 | 138.3 | 281 | 162 | 323.6 | 185.5 | 366 |
| 92 | 197.6 | 115.5 | 240 | 138.8 | 282 | 162.2 | 324 | 186 | 366.8 |
| 92.2 | 198 | 116 | 240.8 | 139 | 282.2 | 162.7 | 325 | 186.1 | 367 |
| 92.7 | 199 | 116.1 | 241 | 139.4 | 283 | 163 | 325.4 | 186.6 | 368 |
| 93 | 199.4 | 116.6 | 242 | 140 | 284 | 163.3 | 326 | 187 | 368.6 |
| 93.3 | 200 | 117 | 242.6 | 140.5 | 285 | 163.8 | 327 | 187.2 | 369 |
| 93.8 | 201 | 117.2 | 243 | 141 | 285.8 | 164 | 327.2 | 187.7 | 370 |
| 94 | 201.2 | 117.7 | 244 | 141.1 | 286 | 164.4 | 328 | 188 | 370.4 |
| 94.4 | 202 | 118 | 244.4 | 141.6 | 287 | 165 | 329 | 188.3 | 371 |
| 95 | 203 | 118.3 | 245 | 142 | 287.6 | 165.5 | 330 | 188.8 | 372 |

*Thermometric Equivalents.*—Continued.

| C.° | F.° | C.° | F.° | C.° | F.° | C.° | F.° | C.° | F.° |
|---|---|---|---|---|---|---|---|---|---|
| 189 | 372.2 | 211.6 | 413 | 233.8 | 453 | 256.1 | 493 | 278.3 | 533 |
| 189.4 | 373 | 212 | 413.6 | 234 | 453.2 | 256.6 | 494 | 278.8 | 534 |
| 190 | 374 | 212.2 | 414 | 234.4 | 454 | 257 | 494.6 | 279 | 534.2 |
| 190.5 | 375 | 212.7 | 415 | 235 | 455 | 257.2 | 495 | 279.4 | 535 |
| 191 | 375.8 | 213 | 415.4 | 235.5 | 456 | 257.7 | 496 | 280 | 536 |
| 191.1 | 376 | 213.3 | 416 | 236 | 456.8 | 258 | 496.4 | 280.5 | 537 |
| 191.6 | 377 | 213.8 | 417 | 236.1 | 457 | 258.3 | 497 | 281 | 537.8 |
| 192 | 377.6 | 214 | 417.2 | 236.6 | 458 | 258.8 | 498 | 281.1 | 538 |
| 192.2 | 378 | 214.4 | 418 | 237 | 458.6 | 259 | 498.2 | 281.6 | 539 |
| 192.7 | 379 | 215 | 419 | 237.2 | 459 | 259 4 | 499 | 282 | 539.6 |
| 193 | 379.4 | 215.5 | 420 | 237.7 | 460 | 260 | 500 | 282.2 | 540 |
| 193.3 | 380 | 216 | 420.8 | 238 | 460.4 | 260.5 | 501 | 282.7 | 541 |
| 193.8 | 381 | 216.1 | 421 | 238.3 | 461 | 261 | 501.8 | 283 | 541.4 |
| 194 | 381.2 | 216.6 | 422 | 238.8 | 462 | 261.1 | 502 | 283.3 | 542 |
| 194.4 | 382 | 217 | 422 6 | 239 | 462.2 | 261.6 | 503 | 283.8 | 543 |
| 195 | 383 | 217.2 | 423 | 239.4 | 463 | 262 | 503.6 | 284 | 543 2 |
| 195.5 | 384 | 217.7 | 424 | 240 | 464 | 262.2 | 504 | 284.4 | 544 |
| 196 | 384.8 | 218 | 424.4 | 240.5 | 465 | 262.7 | 505 | 285 | 545 |
| 196 1 | 385 | 218.3 | 425 | 241 | 465.8 | 263 | 505.4 | 285.5 | 546 |
| 196.6 | 386 | 218.8 | 426 | 241.1 | 466 | 263.3 | 506 | 286 | 546.8 |
| 197 | 386.6 | 219 | 426.2 | 241.6 | 467 | 263.8 | 507 | 286.1 | 547 |
| 197.2 | 387 | 219.4 | 427 | 242 | 467.6 | 264 | 507.2 | 286.6 | 548 |
| 197.7 | 388 | 220 | 428 | 242.2 | 468 | 264.4 | 508 | 287 | 548.6 |
| 198 | 388.4 | 220.5 | 429 | 242.7 | 469 | 265 | 509 | 287.2 | 549 |
| 198.3 | 389 | 221 | 429.8 | 243 | 469.4 | 265.5 | 510 | 287.7 | 550 |
| 198.8 | 390 | 221.1 | 430 | 243.3 | 470 | 266 | 510.8 | 288 | 550.4 |
| 199 | 390.2 | 221.6 | 431 | 243.8 | 471 | 266.1 | 511 | 288.3 | 551 |
| 199.4 | 391 | 222 | 431.6 | 244 | 471.2 | 266.6 | 512 | 288.8 | 552 |
| 200 | 392 | 222.2 | 432 | 244 4 | 472 | 267 | 512.6 | 289 | 552.2 |
| 200.5 | 393 | 222.7 | 433 | 245 | 473 | 267.2 | 513 | 289.4 | 553 |
| 201 | 393.8 | 223 | 433.4 | 245.5 | 474 | 267.7 | 514 | 290 | 554 |
| 201.1 | 394 | 223.3 | 434 | 246 | 474.8 | 268 | 514.4 | 290.5 | 555 |
| 201.6 | 395 | 223.8 | 435 | 246.1 | 475 | 268.3 | 515 | 291 | 555.8 |
| 202 | 395.6 | 224 | 435.2 | 246.6 | 476 | 268.8 | 516 | 291.1 | 556 |
| 202.2 | 396 | 224.4 | 436 | 247 | 476.6 | 269 | 516.2 | 291.6 | 557 |
| 202.7 | 397 | 225 | 437 | 247.2 | 477 | 269.4 | 517 | 292 | 557.6 |
| 203 | 397.4 | 225.5 | 438 | 247.7 | 478 | 270 | 518 | 292.2 | 558 |
| 203.3 | 398 | 226 | 438.8 | 248 | 478.4 | 270.5 | 519 | 292.7 | 559 |
| 203.8 | 399 | 226.1 | 439 | 248.3 | 479 | 271 | 519.8 | 293 | 559.4 |
| 204 | 399.2 | 226.6 | 440 | 248.8 | 480 | 271.1 | 520 | 293.3 | 560 |
| 204.4 | 400 | 227 | 440.6 | 249 | 480.2 | 271.6 | 521 | 293.8 | 561 |
| 205 | 401 | 227.2 | 441 | 249.4 | 481 | 272 | 521.6 | 294 | 561.2 |
| 205.5 | 402 | 227.7 | 442 | 250 | 482 | 272.2 | 522 | 294.4 | 562 |
| 206 | 402.8 | 228 | 442.4 | 250.5 | 483 | 272.7 | 523 | 295 | 563 |
| 206.1 | 403 | 228.3 | 443 | 251 | 483.8 | 273 | 523.4 | 295.5 | 564 |
| 206.6 | 404 | 228.8 | 444 | 251.1 | 484 | 273.3 | 524 | 296 | 564.8 |
| 207 | 404.6 | 229 | 444.2 | 251.6 | 485 | 273.8 | 525 | 296.1 | 565 |
| 207.2 | 405 | 229.4 | 445 | 252 | 485.6 | 274 | 525.2 | 296.6 | 566 |
| 207.7 | 406 | 230 | 446 | 252.2 | 486 | 274.4 | 526 | 297 | 566.6 |
| 208 | 406.4 | 230.5 | 447 | 252.7 | 487 | 275 | 527 | 297.2 | 567 |
| 208.3 | 407 | 231 | 447.8 | 253 | 487.4 | 275.5 | 528 | 297.7 | 568 |
| 208.8 | 408 | 231.1 | 448 | 253.3 | 488 | 276 | 528.8 | 298 | 568.4 |
| 209 | 408.2 | 231.6 | 449 | 253.8 | 489 | 276.1 | 529 | 298.3 | 569 |
| 209.4 | 409 | 232 | 449.6 | 254 | 489.2 | 276.6 | 530 | 298.8 | 570 |
| 210 | 410 | 232.2 | 450 | 254.4 | 490 | 277 | 530.6 | 299 | 570.2 |
| 210.5 | 411 | 232.7 | 451 | 255 | 491 | 277.2 | 531 | 299.4 | 571 |
| 211 | 411.8 | 233 | 451.4 | 255.5 | 492 | 277.7 | 532 | 300 | 572 |
| 211.1 | 412 | 233.3 | 452 | 256 | 492.8 | 278 | 532.4 | | |

## III. Specific Gravity Tables.

### 1. *Baumé's Scale for Liquids Lighter than Water.*

The following table is calculated for a temperature of 17.5° C. (63.5° F.), and is based on the formulas $\frac{140}{B.° + 130}$ = specific gravity and $\frac{140}{\text{specific gravity}}$ — 130 = B.°.

| Degree Baumé. | Specific gravity. | Degree Baumé. | Specific gravity. | Degree Baumé. | Specific gravity. | Degree Baumé. | Specific gravity. |
|---|---|---|---|---|---|---|---|
| 10 | 1.0000 | 33 | 0.8588 | 56 | 0.7526 | 79 | 0.6698 |
| 11 | 0.9929 | 34 | 0.8536 | 57 | 0.7486 | 80 | 0.6666 |
| 12 | 0.9859 | 35 | 0.8484 | 58 | 0.7446 | 81 | 0.6635 |
| 13 | 0.9790 | 36 | 0.8433 | 59 | 0.7407 | 82 | 0.6604 |
| 14 | 0.9722 | 37 | 0.8383 | 60 | 0.7368 | 83 | 0.6573 |
| 15 | 0.9655 | 38 | 0.8333 | 61 | 0.7329 | 84 | 0.6542 |
| 16 | 0.9589 | 39 | 0.8284 | 62 | 0.7290 | 85 | 0.6511 |
| 17 | 0.9523 | 40 | 0.8235 | 63 | 0.7253 | 86 | 0.6482 |
| 18 | 0.9459 | 41 | 0.8187 | 64 | 0.7216 | 87 | 0.6452 |
| 19 | 0.9395 | 42 | 0.8139 | 65 | 0.7179 | 88 | 0.6422 |
| 20 | 0.9333 | 43 | 0.8092 | 66 | 0.7142 | 89 | 0.6393 |
| 21 | 0.9271 | 44 | 0.8045 | 67 | 0.7106 | 90 | 0.6363 |
| 22 | 0.9210 | 45 | 0.8000 | 68 | 0.7070 | 91 | 0.6335 |
| 23 | 0.9150 | 46 | 0.7954 | 69 | 0.7035 | 92 | 0.6306 |
| 24 | 0.9090 | 47 | 0.7909 | 70 | 0.7000 | 93 | 0.6278 |
| 25 | 0.9032 | 48 | 0.7865 | 71 | 0.6965 | 94 | 0.6250 |
| 26 | 0.8974 | 49 | 0.7821 | 72 | 0.6931 | 95 | 0.6222 |
| 27 | 0.8917 | 50 | 0.7777 | 73 | 0.6896 | 96 | 0.6195 |
| 28 | 0.8860 | 51 | 0.7734 | 74 | 0.6863 | 97 | 0.6167 |
| 29 | 0.8805 | 52 | 0.7692 | 75 | 0.6829 | 98 | 0.6140 |
| 30 | 0.8750 | 53 | 0.7650 | 76 | 0.6796 | 99 | 0.6113 |
| 31 | 0.8695 | 54 | 0.7608 | 77 | 0.6763 | 100 | 0.6087 |
| 32 | 0.8641 | 55 | 0.7567 | 78 | 0.6731 | | |

The coefficient of expansion of petroleum oils for increase or decrease of 1° C. in temperature has been determined for both Russian and American oils. For the latter the following figures have been given (Iron Age, xxxviii. No. 7):

| Specific gravity at 15° C. (59° F.). | Coefficient of expansion for 1° C. |
|---|---|
| Under 0.700 | 0.00090 |
| 0.700 to 0.750 | 0.00085 |
| 0.750 to 0.800 | 0.00080 |
| 0.800 to 0.815 | 0.00070 |
| Over 0.815 | 0.00065 |

As stated in the text (p. 34), it is customary in practice to take as the coefficient of expansion 0.004 for every 10° F. (0.00072 for 1° C.).

## 2. *Baumé and Beck's Scales for Liquids Heavier than Water.*

| Degrees. | Baumé, 17.5° C. | Rational Baumé scale, 12.5° C. | Beck, 12.5° C. | Degrees. | Baumé, 17.5° C. | Rational Baumé scale, 12.5° C. | Beck, 12.5° C. |
|---|---|---|---|---|---|---|---|
| | Sp. gr. | Sp. gr. | Sp. gr. | | Sp. gr. | Sp. gr. | Sp. gr. |
| 0 | 1.0000 | 1.0000 | 1.0000 | 37 | 1.3370 | 1.3447 | 1.2782 |
| 1 | 1.0068 | 1.0069 | 1.0059 | 38 | 1.3494 | 1.3574 | 1.2879 |
| 2 | 1.0138 | 1.0140 | 1.0119 | 39 | 1.3619 | 1.3703 | 1.2977 |
| 3 | 1.0208 | 1.0212 | 1.0180 | 40 | 1.3746 | 1.3834 | 1.3077 |
| 4 | 1.0280 | 1.0285 | 1.0241 | 41 | 1.3876 | 1.3968 | 1.3178 |
| 5 | 1.0353 | 1.0358 | 1.0303 | 42 | 1.4009 | 1.4105 | 1.3281 |
| 6 | 1.0426 | 1.0434 | 1.0366 | 43 | 1.4143 | 1.4244 | 1.3386 |
| 7 | 1.0501 | 1.0509 | 1.0429 | 44 | 1.4281 | 1.4386 | 1.3492 |
| 8 | 1.0576 | 1.0587 | 1.0494 | 45 | 1.4421 | 1.4531 | 1.3600 |
| 9 | 1.0653 | 1.0665 | 1.0559 | 46 | 1.4564 | 1.4678 | 1.3710 |
| 10 | 1.0731 | 1.0745 | 1.0625 | 47 | 1.4710 | 1.4828 | 1.3821 |
| 11 | 1.0810 | 1.0825 | 1.0692 | 48 | 1.4860 | 1.4984 | 1.3934 |
| 12 | 1.0890 | 1.0907 | 1 0759 | 49 | 1.5012 | 1.5141 | 1.4050 |
| 13 | 1.0972 | 1.0990 | 1.0828 | 50 | 1.5167 | 1.5301 | 1.3167 |
| 14 | 1.1054 | 1.1074 | 1.0897 | 51 | 1.5325 | 1.5466 | 1.4286 |
| 15 | 1.1138 | 1.1160 | 1.0968 | 52 | 1.5487 | 1.5633 | 1.4407 |
| 16 | 1.1224 | 1.1247 | 1.1031 | 53 | 1.5652 | 1.5804 | 1.4530 |
| 17 | 1.1310 | 1.1335 | 1.1119 | 54 | 1.5820 | 1.5978 | 1.4655 |
| 18 | 1.1398 | 1.1425 | 1.1184 | 55 | 1.5993 | 1.6158 | 1.4783 |
| 19 | 1.1487 | 1.1516 | 1.1258 | 56 | 1.6169 | 1.6342 | 1.4912 |
| 20 | 1.1578 | 1.1608 | 1.1333 | 57 | 1.6349 | 1.6529 | 1.5044 |
| 21 | 1.1670 | 1.1702 | 1.1409 | 58 | 1.6533 | 1.6720 | 1.5179 |
| 22 | 1.1763 | 1.1798 | 1.1486 | 59 | 1.6721 | 1.6916 | 1.5315 |
| 23 | 1.1858 | 1.1896 | 1.1565 | 60 | 1.6914 | 1.7116 | 1 5434 |
| 24 | 1.1955 | 1.1994 | 1.1644 | 61 | 1.7111 | 1.7322 | 1.5596 |
| 25 | 1.2053 | 1.2095 | 1.1724 | 62 | 1.7313 | 1.7532 | 1.5741 |
| 26 | 1.2153 | 1.2198 | 1.1806 | 63 | 1.7520 | 1.7748 | 1.5888 |
| 27 | 1.2254 | 1.2301 | 1.1888 | 64 | 1.7731 | 1.7960 | 1.6038 |
| 28 | 1.2357 | 1.2407 | 1.1972 | 65 | 1.7948 | 1.8195 | 1.6190 |
| 29 | 1.2462 | 1.2515 | 1.2057 | 66 | 1.8171 | 1.8428 | 1.6346 |
| 30 | 1.2569 | 1.2624 | 1.2143 | 67 | 1.8398 | 1.839 | 1.6505 |
| 31 | 1.2677 | 1.2736 | 1.2230 | 68 | 1.8632 | 1.864 | 1.6667 |
| 32 | 1.2788 | 1.2849 | 1.2319 | 69 | 1.8871 | 1.885 | 1.6832 |
| 33 | 1.2901 | 1.2965 | 1.2409 | 70 | 1.9117 | 1.909 | 1.7000 |
| 34 | 1.3015 | 1.3082 | 1.2500 | 71 | 1.9370 | 1.935 | 1.7272 |
| 35 | 1.3131 | 1.3202 | 1.2593 | 72 | 1.9629 | 1.960 | 1.7347 |
| 36 | 1.3250 | 1.3324 | 1.2687 | | | | |

What is known as the "Rational" Baumé scale is calculated by taking water at the temperature chosen at 0° B. and sulphuric acid of 1.842 specific gravity at 66° B. and using the formula $\frac{144.3}{144.3 - n^\circ} = d$. (See Lunge's "Sulphuric Acid and Alkali," vol. i. p. 20.)

### 3. *Twaddle's Scale for Liquids Heavier than Water.*

| Degrees Twaddle. | Specific gravity. | Degrees Twaddle. | Specific gravity. | Degrees Twaddle. | Specific gravity. | Degrees Twaddle. | Specific gravity. | Degrees Twaddle. | Specific gravity. | Degrees Twaddle. | Specific gravity. | Degrees Twaddle. | Specific gravity. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 1.000 | 29 | 1.145 | 58 | 1.290 | 87 | 1.435 | 116 | 1.580 | 145 | 1.725 | 173 | 1.865 |
| 1 | 1.005 | 30 | 1.150 | 59 | 1.295 | 88 | 1.440 | 117 | 1.585 | 146 | 1.730 | 174 | 1.870 |
| 2 | 1.010 | 31 | 1.155 | 60 | 1.300 | 89 | 1.445 | 118 | 1.590 | 147 | 1.735 | 175 | 1.875 |
| 3 | 1.015 | 32 | 1.160 | 61 | 1.305 | 90 | 1.450 | 119 | 1.595 | 148 | 1.740 | 176 | 1.880 |
| 4 | 1.020 | 33 | 1.165 | 62 | 1.310 | 91 | 1.455 | 120 | 1.600 | 149 | 1.745 | 177 | 1.885 |
| 5 | 1.025 | 34 | 1.170 | 63 | 1.315 | 92 | 1.460 | 121 | 1.605 | 150 | 1.750 | 178 | 1.890 |
| 6 | 1.030 | 35 | 1.175 | 64 | 1.320 | 93 | 1.465 | 122 | 1.610 | 151 | 1.755 | 179 | 1.895 |
| 7 | 1.035 | 36 | 1.180 | 65 | 1.325 | 94 | 1.470 | 123 | 1.615 | 152 | 1.760 | 180 | 1.900 |
| 8 | 1.040 | 37 | 1.185 | 66 | 1.330 | 95 | 1.475 | 124 | 1.620 | 153 | 1.765 | 181 | 1.905 |
| 9 | 1.045 | 38 | 1.190 | 67 | 1.335 | 96 | 1.480 | 125 | 1.625 | 154 | 1.770 | 182 | 1.910 |
| 10 | 1.050 | 39 | 1.195 | 68 | 1.340 | 97 | 1.485 | 126 | 1.630 | 155 | 1.775 | 183 | 1.915 |
| 11 | 1.055 | 40 | 1.200 | 69 | 1.345 | 98 | 1.490 | 127 | 1.635 | 156 | 1.780 | 184 | 1.920 |
| 12 | 1.060 | 41 | 1.205 | 70 | 1.350 | 99 | 1.495 | 128 | 1.640 | 157 | 1.785 | 185 | 1.925 |
| 13 | 1.065 | 42 | 1.210 | 71 | 1.355 | 100 | 1.500 | 129 | 1.645 | 158 | 1.790 | 186 | 1.930 |
| 14 | 1.070 | 43 | 1.215 | 72 | 1.360 | 101 | 1.505 | 130 | 1.650 | 159 | 1.795 | 187 | 1.935 |
| 15 | 1.075 | 44 | 1.220 | 73 | 1.365 | 102 | 1.510 | 131 | 1.655 | 160 | 1.800 | 188 | 1.940 |
| 16 | 1.080 | 45 | 1.225 | 74 | 1.370 | 103 | 1.515 | 132 | 1.660 | 161 | 1.805 | 189 | 1.945 |
| 17 | 1.085 | 46 | 1.230 | 75 | 1.375 | 104 | 1.520 | 133 | 1.665 | 162 | 1.810 | 190 | 1.950 |
| 18 | 1.090 | 47 | 1.235 | 76 | 1.380 | 105 | 1.525 | 134 | 1.670 | 163 | 1.815 | 191 | 1.955 |
| 19 | 1.095 | 48 | 1.240 | 77 | 1.385 | 106 | 1.530 | 135 | 1.675 | 164 | 1.820 | 192 | 1.960 |
| 20 | 1.100 | 49 | 1.245 | 78 | 1.390 | 107 | 1.535 | 136 | 1.680 | 165 | 1.825 | 193 | 1.965 |
| 21 | 1.105 | 50 | 1.250 | 79 | 1.395 | 108 | 1.540 | 137 | 1.685 | 166 | 1.830 | 194 | 1.970 |
| 22 | 1.110 | 51 | 1.255 | 80 | 1.400 | 109 | 1.545 | 138 | 1.690 | 167 | 1.835 | 195 | 1.975 |
| 23 | 1.115 | 52 | 1.260 | 81 | 1.405 | 110 | 1.550 | 139 | 1.695 | 168 | 1.840 | 196 | 1.980 |
| 24 | 1.120 | 53 | 1.265 | 82 | 1.410 | 111 | 1.555 | 140 | 1.700 | 169 | 1.845 | 197 | 1.985 |
| 25 | 1.125 | 54 | 1.270 | 83 | 1.415 | 112 | 1.560 | 141 | 1.705 | 170 | 1.850 | 198 | 1.990 |
| 26 | 1.130 | 55 | 1.275 | 84 | 1.420 | 113 | 1.565 | 142 | 1.710 | 171 | 1.855 | 199 | 1.995 |
| 27 | 1.135 | 56 | 1.280 | 85 | 1.425 | 114 | 1.570 | 143 | 1.715 | 172 | 1.860 | 200 | 2.000 |
| 28 | 1.140 | 57 | 1.285 | 86 | 1.430 | 115 | 1.575 | 144 | 1.720 | | | | |

The uniform division of the Twaddle scale makes the degrees very easily convertible into specific gravity readings. It is only necessary to multiply the degree as read off by five and add this to 1.000 in order to obtain the specific gravity.

Again, as the gallon of distilled water at ordinary temperatures weighs ten pounds avoirdupois, it is possible to determine the weight of a gallon of an acid or lye by the aid of the Twaddle scale. Thus, if an acid shows 50° Twaddle, corresponding to the specific gravity 1.250, it weighs twelve and a half pounds per gallons. Or, as a litre of distilled water weighs one thousand grammes, a litre of a liquid showing 20° Twaddle will weigh eleven hundred grammes.

### 4. *Comparison of the Twaddle Scale with the Rational Baumé Scale.*

| Twaddle. | Baumé. | Specific gravity. | Twaddle. | Baumé. | Specific gravity. | Twaddle. | Baumé. | Specific gravity. | Twaddle. | Baumé. | Specific gravity. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 1.000 | 44 | 26.0 | 1.220 | 88 | 44.1 | 1.440 | 131 | 57.1 | 1.655 |
| 1 | 0.7 | 1.005 | 45 | 26.4 | 1.225 | 89 | 44.4 | 1.445 | 132 | 57.4 | 1.660 |
| 2 | 1.4 | 1.010 | 46 | 26.9 | 1.230 | 90 | 44.8 | 1.450 | 133 | 57.7 | 1.665 |
| 3 | 2.1 | 1.015 | 47 | 27.4 | 1.235 | 91 | 45.1 | 1.455 | 134 | 57.9 | 1.670 |
| 4 | 2.7 | 1.020 | 48 | 27.9 | 1.240 | 92 | 45.4 | 1.460 | 135 | 58.2 | 1.675 |
| 5 | 3.4 | 1.025 | 49 | 28.4 | 1.245 | 93 | 45.8 | 1.465 | 136 | 58.4 | 1.680 |
| 6 | 4.1 | 1.030 | 50 | 28.8 | 1.250 | 94 | 46.1 | 1.470 | 137 | 58.7 | 1.685 |
| 7 | 4.7 | 1.035 | 51 | 29.3 | 1.255 | 95 | 46.4 | 1.475 | 138 | 58.9 | 1.690 |
| 8 | 5.4 | 1.040 | 52 | 29.7 | 1.260 | 96 | 46.8 | 1.480 | 139 | 59.2 | 1.695 |
| 9 | 6.0 | 1.045 | 53 | 30.2 | 1.265 | 97 | 47.1 | 1.485 | 140 | 59.5 | 1.700 |
| 10 | 6.7 | 1.050 | 54 | 30.6 | 1.270 | 98 | 47.4 | 1.490 | 141 | 59.7 | 1.705 |
| 11 | 7.4 | 1.055 | 55 | 31.1 | 1.275 | 99 | 47.8 | 1.495 | 142 | 60.0 | 1.710 |
| 12 | 8.0 | 1.060 | 56 | 31.5 | 1.280 | 100 | 48.1 | 1.500 | 143 | 60.2 | 1.715 |
| 13 | 8.7 | 1.065 | 57 | 32.0 | 1.285 | 101 | 48.4 | 1.505 | 144 | 60.4 | 1.720 |
| 14 | 9.4 | 1.070 | 58 | 32.4 | 1.290 | 102 | 48.7 | 1.510 | 145 | 60.6 | 1.725 |
| 15 | 10.0 | 1.075 | 59 | 32.8 | 1.295 | 103 | 49.0 | 1.515 | 146 | 60.9 | 1.730 |
| 16 | 10.6 | 1.080 | 60 | 33.3 | 1.300 | 104 | 49.4 | 1.520 | 147 | 61.1 | 1.735 |
| 17 | 11.2 | 1.085 | 61 | 33.7 | 1.305 | 105 | 49.7 | 1.525 | 148 | 61.4 | 1.740 |
| 18 | 11.9 | 1.090 | 62 | 34.2 | 1.310 | 106 | 50.0 | 1.530 | 149 | 61.6 | 1.745 |
| 19 | 12.4 | 1.095 | 63 | 34.6 | 1.315 | 107 | 50.3 | 1.535 | 150 | 61.8 | 1.750 |
| 20 | 13.0 | 1.100 | 64 | 35.0 | 1.320 | 108 | 50.6 | 1.540 | 151 | 62.1 | 1.755 |
| 21 | 13.6 | 1.105 | 65 | 35.4 | 1.325 | 109 | 50.9 | 1.545 | 152 | 62.3 | 1.760 |
| 22 | 14.2 | 1.110 | 66 | 35.8 | 1.330 | 110 | 51.2 | 1.550 | 153 | 62.5 | 1.765 |
| 23 | 14.9 | 1.115 | 67 | 36.2 | 1.335 | 111 | 51.5 | 1.555 | 154 | 62.8 | 1.770 |
| 24 | 15.4 | 1.120 | 68 | 36.6 | 1.340 | 112 | 51.8 | 1.560 | 155 | 63.0 | 1.775 |
| 25 | 16.0 | 1.125 | 69 | 37.0 | 1.345 | 113 | 52.1 | 1.565 | 156 | 63.2 | 1.780 |
| 26 | 16.5 | 1.130 | 70 | 37.4 | 1.350 | 114 | 52.4 | 1.570 | 157 | 63.5 | 1.785 |
| 27 | 17.1 | 1.135 | 71 | 37.8 | 1.355 | 115 | 52.7 | 1.575 | 158 | 63.7 | 1.790 |
| 28 | 17.7 | 1.140 | 72 | 38.2 | 1.360 | 116 | 53.0 | 1.580 | 159 | 64.0 | 1.795 |
| 29 | 18.3 | 1.145 | 73 | 38.6 | 1.365 | 117 | 53.3 | 1.585 | 160 | 64.2 | 1.800 |
| 30 | 18.8 | 1.150 | 74 | 39.0 | 1.370 | 118 | 53.6 | 1.590 | 161 | 64.4 | 1.805 |
| 31 | 19.3 | 1.155 | 75 | 39.4 | 1.375 | 119 | 53.9 | 1.595 | 162 | 64.6 | 1.810 |
| 32 | 19.8 | 1.160 | 76 | 39.8 | 1.380 | 120 | 54.1 | 1.600 | 163 | 64.8 | 1.815 |
| 33 | 20.3 | 1.165 | 77 | 40.1 | 1.385 | 121 | 54.4 | 1.605 | 164 | 65.0 | 1.820 |
| 34 | 20.9 | 1.170 | 78 | 40.5 | 1.390 | 122 | 54.7 | 1.610 | 165 | 65.2 | 1.825 |
| 35 | 21.4 | 1.175 | 79 | 40.8 | 1.395 | 123 | 55.0 | 1.615 | 166 | 65.5 | 1.830 |
| 36 | 22.0 | 1.180 | 80 | 41.2 | 1.400 | 124 | 55.2 | 1.620 | 167 | 65.7 | 1.835 |
| 37 | 22.5 | 1.185 | 81 | 41.6 | 1.405 | 125 | 55.5 | 1.625 | 168 | 65.9 | 1.840 |
| 38 | 23.0 | 1.190 | 82 | 42.0 | 1.410 | 126 | 55.8 | 1.630 | 169 | 66.1 | 1.845 |
| 39 | 23.5 | 1.195 | 83 | 42.3 | 1.415 | 127 | 56.0 | 1.635 | 170 | 66.3 | 1.850 |
| 40 | 24.0 | 1.200 | 84 | 42.7 | 1.420 | 128 | 56.3 | 1.640 | 171 | 66.5 | 1.855 |
| 41 | 24.5 | 1.205 | 85 | 43.1 | 1.425 | 129 | 56.6 | 1.645 | 172 | 66.7 | 1.860 |
| 42 | 25.0 | 1.210 | 86 | 43.4 | 1.430 | 130 | 56.9 | 1.650 | 173 | 67.0 | 1.865 |
| 43 | 25.5 | 1.215 | 87 | 43.8 | 1.435 | | | | | | |

## 5. *Comparison of Gay-Lussac Scale with Absolute Specific Gravity Figures.*

| Degree. | Specific gravity, Gay-Lussac. | Degree. | Specific gravity, Gay-Lussac. | Degree. | Specific gravity, Gay-Lussac. | Degree. | Specific gravity, Gay-Lussac. |
|---|---|---|---|---|---|---|---|
| 50 | 2.0000 | 76 | 1.3158 | 102 | 0.9804 | 127 | 0.7874 |
| 51 | 1.9608 | 77 | 1.2987 | 103 | 0.9709 | 128 | 0.7813 |
| 52 | 1.9231 | 78 | 1.2821 | 104 | 0.9615 | 129 | 0.7752 |
| 53 | 1.8868 | 79 | 1.2658 | 105 | 0.9524 | 130 | 0.7692 |
| 54 | 1.8519 | 80 | 1.2500 | 106 | 0.9434 | 131 | 0.7634 |
| 55 | 1.8182 | 81 | 1 2346 | 107 | 0.9346 | 132 | 0.7576 |
| 56 | 1.7857 | 82 | 1.2195 | 108 | 0.9259 | 133 | 0.7519 |
| 57 | 1.7544 | 83 | 1.2048 | 109 | 0.9174 | 134 | 0.7463 |
| 58 | 1.7241 | 84 | 1.1905 | 110 | 0.9091 | 135 | 0.7408 |
| 59 | 1.6949 | 85 | 1.1765 | 111 | 0.9009 | 136 | 0.7353 |
| 60 | 1.6667 | 86 | 1.1628 | 112 | 0.8929 | 137 | 0.7299 |
| 61 | 1.6393 | 87 | 1.1494 | 113 | 0.8850 | 138 | 0.7246 |
| 62 | 1.6129 | 88 | 1.1364 | 114 | 0.8772 | 139 | 0.7194 |
| 63 | 1.5873 | 89 | 1.1236 | 115 | 0.8696 | 140 | 0.7143 |
| 64 | 1.5625 | 90 | 1.1111 | 116 | 0.8621 | 141 | 0.7092 |
| 65 | 1.5385 | 91 | 1.0989 | 117 | 0.8547 | 142 | 0.7042 |
| 66 | 1.5152 | 92 | 1.0870 | 118 | 0.8475 | 143 | 0.6993 |
| 67 | 1.4925 | 93 | 1.0753 | 119 | 0.8403 | 144 | 0.6944 |
| 68 | 1.4706 | 94 | 1.0638 | 120 | 0.8333 | 145 | 0.6897 |
| 69 | 1.4493 | 95 | 1.0526 | 121 | 0.8264 | 146 | 0.6850 |
| 70 | 1.4286 | 96 | 1.0417 | 122 | 0.8197 | 147 | 0.6803 |
| 71 | 1.4085 | 97 | 1.0309 | 123 | 0.8130 | 148 | 0.6757 |
| 72 | 1.3889 | 98 | 1.0204 | 124 | 0.8065 | 149 | 0.6711 |
| 73 | 1.3699 | 99 | 1.0101 | 125 | 0.8000 | 150 | 0.6667 |
| 74 | 1.3514 | 100 | 1.0000 | 126 | 0.7937 | | |
| 75 | 1.3333 | 101 | 0.9901 | | | | |

### 6. *Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix (as used for sugar solutions).*

| Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. |
|---|---|---|---|---|---|---|---|---|
| 0.0 | 1.00000 | 0.00 | 5.0 | 1.01970 | 2.84 | 10.0 | 1.04014 | 5.67 |
| 0.1 | 1.00038 | 0.06 | 5.1 | 1.02010 | 2.89 | 10.1 | 1.04055 | 5.72 |
| 0.2 | 1.00077 | 0.11 | 5.2 | 1.02051 | 2.95 | 10.2 | 1.04097 | 5.78 |
| 0.3 | 1.00116 | 0.17 | 5.3 | 1.02091 | 3.01 | 10.3 | 1.04139 | 5.83 |
| 0.4 | 1.00155 | 0.23 | 5.4 | 1.02131 | 3.06 | 10.4 | 1.04180 | 5.89 |
| 0.5 | 1.00193 | 0.28 | 5.5 | 1.02171 | 3.12 | 10.5 | 1.04222 | 5.95 |
| 0.6 | 1.00232 | 0.34 | 5.6 | 1.02211 | 3.18 | 10.6 | 1.04264 | 6.00 |
| 0.7 | 1.00271 | 0.40 | 5.7 | 1.02252 | 3.23 | 10.7 | 1.04306 | 6.06 |
| 0.8 | 1.00310 | 0.45 | 5.8 | 1.02292 | 3.29 | 10.8 | 1.04348 | 6.12 |
| 0.9 | 1.00349 | 0.51 | 5.9 | 1.02333 | 3.35 | 10.9 | 1.04390 | 6.17 |
| 1.0 | 1.00388 | 0.57 | 6.0 | 1.02373 | 3.40 | 11.0 | 1.04431 | 6.23 |
| 1.1 | 1.00427 | 0.63 | 6.1 | 1.02413 | 3.46 | 11.1 | 1.04473 | 6.29 |
| 1.2 | 1.00466 | 0.68 | 6.2 | 1.02454 | 3.52 | 11.2 | 1.04515 | 6.34 |
| 1.3 | 1.00505 | 0.74 | 6.3 | 1.02494 | 3.57 | 11.3 | 1.04557 | 6.40 |
| 1.4 | 1.00544 | 0.80 | 6.4 | 1.02535 | 3.63 | 11.4 | 1.04599 | 6.46 |
| 1.5 | 1.00583 | 0.85 | 6.5 | 1.02575 | 3.69 | 11.5 | 1.04641 | 6.51 |
| 1.6 | 1.00622 | 0.91 | 6.6 | 1.02616 | 3.74 | 11.6 | 1.04683 | 6.57 |
| 1.7 | 1.00662 | 0.97 | 6.7 | 1.02657 | 3.80 | 11.7 | 1.04726 | 6.62 |
| 1.8 | 1.00701 | 1.02 | 6.8 | 1.02697 | 3.86 | 11.8 | 1.04768 | 6.68 |
| 1.9 | 1.00740 | 1.08 | 6.9 | 1.02738 | 3.91 | 11.9 | 1.04810 | 6.74 |
| 2.0 | 1.00779 | 1.14 | 7.0 | 1.02779 | 3.97 | 12.0 | 1.04852 | 6.79 |
| 2.1 | 1.00818 | 1.19 | 7.1 | 1.02819 | 4.03 | 12.1 | 1.04894 | 6.85 |
| 2.2 | 1.00858 | 1.25 | 7.2 | 1.02860 | 4.08 | 12.2 | 1.04937 | 6.91 |
| 2.3 | 1.00897 | 1.31 | 7.3 | 1.02901 | 4.14 | 12.3 | 1.04979 | 6.96 |
| 2.4 | 1.00936 | 1.36 | 7.4 | 1.02942 | 4.20 | 12.4 | 1.05021 | 7.02 |
| 2.5 | 1.00976 | 1.42 | 7.5 | 1.02983 | 4.25 | 12.5 | 1.05064 | 7.08 |
| 2.6 | 1.01015 | 1.48 | 7.6 | 1.03024 | 4.31 | 12.6 | 1.05106 | 7.13 |
| 2.7 | 1.01055 | 1.53 | 7.7 | 1.03064 | 4.37 | 12.7 | 1.05149 | 7.19 |
| 2.8 | 1.01094 | 1.59 | 7.8 | 1.03105 | 4.42 | 12.8 | 1.05191 | 7.24 |
| 2.9 | 1.01134 | 1.65 | 7.9 | 1.03146 | 4.48 | 12.9 | 1.05233 | 7.30 |
| 3.0 | 1.01173 | 1.70 | 8.0 | 1.03187 | 4.53 | 13.0 | 1.05276 | 7.36 |
| 3.1 | 1.01213 | 1.76 | 8.1 | 1.03228 | 4.59 | 13.1 | 1.05318 | 7.41 |
| 3.2 | 1.01252 | 1.82 | 8.2 | 1.03270 | 4.65 | 13.2 | 1.05361 | 7.47 |
| 3.3 | 1.01292 | 1.87 | 8.3 | 1.03311 | 4.70 | 13.3 | 1.05404 | 7.53 |
| 3.4 | 1.01332 | 1.93 | 8.4 | 1.03352 | 4.76 | 13.4 | 1.05446 | 7.58 |
| 3.5 | 1.01371 | 1.99 | 8.5 | 1.03393 | 4.82 | 13.5 | 1.05489 | 7.64 |
| 3.6 | 1.01411 | 2.04 | 8.6 | 1.03434 | 4.87 | 13.6 | 1.05532 | 7.69 |
| 3.7 | 1.01451 | 2.10 | 8.7 | 1.03475 | 4.93 | 13.7 | 1.05574 | 7.75 |
| 3.8 | 1.01491 | 2.16 | 8.8 | 1.03517 | 4.99 | 13.8 | 1.05617 | 7.81 |
| 3.9 | 1.01531 | 2.21 | 8.9 | 1.03558 | 5.04 | 13.9 | 1.05660 | 7.86 |
| 4.0 | 1.01570 | 2.27 | 9.0 | 1.03599 | 5.10 | 14.0 | 1.05703 | 7.92 |
| 4.1 | 1.01610 | 2.33 | 9.1 | 1.03640 | 5.16 | 14.1 | 1.05746 | 7.98 |
| 4.2 | 1.01650 | 2.38 | 9.2 | 1.03682 | 5.21 | 14.2 | 1.05789 | 8.03 |
| 4.3 | 1.01690 | 2.44 | 9.3 | 1.03723 | 5.27 | 14.3 | 1.05831 | 8.09 |
| 4.4 | 1.01730 | 2.50 | 9.4 | 1.03765 | 5.33 | 14.4 | 1.05874 | 8.14 |
| 4.5 | 1.01770 | 2.55 | 9.5 | 1.03806 | 5.38 | 14.5 | 1.05917 | 8.20 |
| 4.6 | 1.01810 | 2.61 | 9.6 | 1.03848 | 5.44 | 14.6 | 1.05960 | 8.26 |
| 4.7 | 1.01850 | 2.67 | 9.7 | 1.03889 | 5.50 | 14.7 | 1.06003 | 8.31 |
| 4.8 | 1.01890 | 2.72 | 9.8 | 1.03931 | 5.55 | 14.8 | 1.06047 | 8.37 |
| 4.9 | 1.01930 | 2.78 | 9.9 | 1.03972 | 5.61 | 14.9 | 1.06090 | 8.43 |

*Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.*—Continued.

| Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. |
|---|---|---|---|---|---|---|---|---|
| 15.0 | 1.06133 | 8.48 | 20.0 | 1.08329 | 11.29 | 25.0 | 1.10607 | 14.08 |
| 15.1 | 1.06176 | 8.54 | 20.1 | 1.08374 | 11.34 | 25.1 | 1.10653 | 14.13 |
| 15.2 | 1.06219 | 8.59 | 20.2 | 1.08419 | 11.40 | 25.2 | 1.10700 | 14.19 |
| 15.3 | 1.06262 | 8.65 | 20.3 | 1.08464 | 11.45 | 25.3 | 1.10746 | 14.24 |
| 15.4 | 1.06306 | 8.71 | 20.4 | 1.08509 | 11.51 | 25.4 | 1.10793 | 14.30 |
| 15.5 | 1.06349 | 8.76 | 20.5 | 1.08553 | 11.57 | 25.5 | 1.10839 | 14.35 |
| 15.6 | 1.06392 | 8.82 | 20.6 | 1.08599 | 11.62 | 25.6 | 1.10886 | 14.41 |
| 15.7 | 1.06436 | 8.88 | 20.7 | 1.08643 | 11.68 | 25.7 | 1.10932 | 14.47 |
| 15.8 | 1.06479 | 8.93 | 20.8 | 1.08688 | 11.73 | 25.8 | 1.10979 | 14.52 |
| 15.9 | 1.06522 | 8.99 | 20.9 | 1.08733 | 11.79 | 25.9 | 1.11026 | 14.58 |
| 16.0 | 1.06566 | 9.04 | 21.0 | 1.08778 | 11.85 | 26.0 | 1.11072 | 14.63 |
| 16.1 | 1.06609 | 9.10 | 21.1 | 1.08824 | 11.90 | 26.1 | 1.11119 | 14.69 |
| 16.2 | 1.06653 | 9.16 | 21.2 | 1.08869 | 11.96 | 26.2 | 1.11166 | 14.74 |
| 16.3 | 1.06696 | 9.21 | 21.3 | 1.08914 | 12.01 | 26.3 | 1.11213 | 14.80 |
| 16.4 | 1.06740 | 9.27 | 21.4 | 1.08959 | 12.07 | 26.4 | 1.11259 | 14.85 |
| 16.5 | 1.06783 | 9.33 | 21.5 | 1.09004 | 12.13 | 26.5 | 1.11306 | 14.91 |
| 16.6 | 1.06827 | 9.38 | 21.6 | 1.09049 | 12.18 | 26.6 | 1.11353 | 14.97 |
| 16.7 | 1.06871 | 9.44 | 21.7 | 1.09095 | 12.24 | 26.7 | 1.11400 | 15.02 |
| 16.8 | 1.06914 | 9.49 | 21.8 | 1.09140 | 12.29 | 26.8 | 1.11447 | 15.08 |
| 16.9 | 1.06958 | 9.55 | 21.9 | 1.09185 | 12.35 | 26.9 | 1.11494 | 15.13 |
| 17.0 | 1.07002 | 9.61 | 22.0 | 1.09231 | 12.40 | 27.0 | 1.11541 | 15.19 |
| 17.1 | 1.07046 | 9.66 | 22.1 | 1.09276 | 12.46 | 27.1 | 1.11588 | 15.24 |
| 17.2 | 1.07090 | 9.72 | 22.2 | 1.09321 | 12.52 | 27.2 | 1.11635 | 15.30 |
| 17.3 | 1.07133 | 9.77 | 22.3 | 1.09367 | 12.57 | 27.3 | 1.11682 | 15.35 |
| 17.4 | 1.07177 | 9.83 | 22.4 | 1.09412 | 12.63 | 27.4 | 1.11729 | 15.41 |
| 17.5 | 1.07221 | 9.89 | 22.5 | 1.09458 | 12.68 | 27.5 | 1.11776 | 15.46 |
| 17.6 | 1.07265 | 9.94 | 22.6 | 1.09503 | 12.74 | 27.6 | 1.11824 | 15.52 |
| 17.7 | 1.07309 | 10.00 | 22.7 | 1.09549 | 12.80 | 27.7 | 1.11871 | 15.58 |
| 17.8 | 1.07353 | 10.06 | 22.8 | 1.09595 | 12.85 | 27.8 | 1.11918 | 15.63 |
| 17.9 | 1.07397 | 10.11 | 22.9 | 1.09640 | 12.91 | 27.9 | 1.11965 | 15.69 |
| 18.0 | 1.07441 | 10.17 | 23.0 | 1.09686 | 12.96 | 28.0 | 1.12013 | 15.74 |
| 18.1 | 1.07485 | 10.22 | 23.1 | 1.09732 | 13.02 | 28.1 | 1.12060 | 15.80 |
| 18.2 | 1.07530 | 10.28 | 23.2 | 1.09777 | 13.07 | 28.2 | 1.12107 | 15.85 |
| 18.3 | 1.07574 | 10.33 | 23.3 | 1.09823 | 13.13 | 28.3 | 1.12155 | 15.91 |
| 18.4 | 1.07618 | 10.39 | 23.4 | 1.09869 | 13.19 | 28.4 | 1.12202 | 15.96 |
| 18.5 | 1.07662 | 10.45 | 23.5 | 1.09915 | 13.24 | 28.5 | 1.12250 | 16.02 |
| 18.6 | 1.07706 | 10.50 | 23.6 | 1.09961 | 13.30 | 28.6 | 1.12297 | 16.07 |
| 18.7 | 1.07751 | 10.56 | 23.7 | 1.10007 | 13.35 | 28.7 | 1.12345 | 16.13 |
| 18.8 | 1.07795 | 10.62 | 23.8 | 1.10053 | 13.41 | 28.8 | 1.12393 | 16.18 |
| 18.9 | 1.07839 | 10.67 | 23.9 | 1.10099 | 13.46 | 28.9 | 1.12440 | 16.24 |
| 19.0 | 1.07884 | 10.73 | 24.0 | 1.10145 | 13.52 | 29.0 | 1.12488 | 16.30 |
| 19.1 | 1.07928 | 10.78 | 24.1 | 1.10191 | 13.58 | 29.1 | 1.12536 | 16.35 |
| 19.2 | 1.07973 | 10.84 | 24.2 | 1.10237 | 13.63 | 29.2 | 1.12583 | 16.41 |
| 19.3 | 1.08017 | 10.90 | 24.3 | 1.10283 | 13.69 | 29.3 | 1.12631 | 16.46 |
| 19.4 | 1.08062 | 10.95 | 24.4 | 1.10329 | 13.74 | 29.4 | 1.12679 | 16.52 |
| 19.5 | 1.08106 | 11.01 | 24.5 | 1.10375 | 13.80 | 29.5 | 1.12727 | 16.57 |
| 19.6 | 1.08151 | 11.06 | 24.6 | 1.10421 | 13.85 | 29.6 | 1.12775 | 16.63 |
| 19.7 | 1.08196 | 11.12 | 24.7 | 1.10468 | 13.91 | 29.7 | 1.12823 | 16.68 |
| 19.8 | 1.08240 | 11.18 | 24.8 | 1.10514 | 13.96 | 29.8 | 1.12871 | 16.74 |
| 19.9 | 1.08285 | 11.27 | 24.9 | 1.10560 | 14.02 | 29.9 | 1.12919 | 16.79 |

*Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.*—Continued.

| Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. |
|---|---|---|---|---|---|---|---|---|
| 30.0 | 1.12967 | 16.85 | 35.0 | 1.15411 | 19.60 | 40.0 | 1.17943 | 22.33 |
| 30.1 | 1.13015 | 16.90 | 35.1 | 1.15461 | 19.66 | 40.1 | 1.17995 | 22.38 |
| 30.2 | 1.13063 | 16.96 | 35.2 | 1.15511 | 19.71 | 40.2 | 1.18046 | 22.44 |
| 30.3 | 1.13111 | 17.01 | 35.3 | 1.15561 | 19.76 | 40.3 | 1.18098 | 22.49 |
| 30.4 | 1.13159 | 17.07 | 35.4 | 1.15611 | 19.82 | 40.4 | 1.18150 | 22.55 |
| 30.5 | 1.13207 | 17.12 | 35.5 | 1.15661 | 19.87 | 40.5 | 1.18201 | 22.60 |
| 30.6 | 1.13255 | 17.18 | 35.6 | 1.15710 | 19.93 | 40.6 | 1.18253 | 22.66 |
| 30.7 | 1.13304 | 17.23 | 35.7 | 1.15760 | 19.98 | 40.7 | 1.18305 | 22.71 |
| 30.8 | 1.13352 | 17.29 | 35.8 | 1.15810 | 20.04 | 40.8 | 1.18357 | 22.77 |
| 30.9 | 1.13400 | 17.35 | 35.9 | 1.15861 | 20.09 | 40.9 | 1.18408 | 22.82 |
| 31.0 | 1.13449 | 17.40 | 36.0 | 1.15911 | 20.15 | 41.0 | 1.18460 | 22.87 |
| 31.1 | 1.13497 | 17.46 | 36.1 | 1.15961 | 20.20 | 41.1 | 1.18512 | 22.93 |
| 31.2 | 1.13545 | 17.51 | 36.2 | 1.16011 | 20.26 | 41.2 | 1.18564 | 22.98 |
| 31.3 | 1.13594 | 17.57 | 36.3 | 1.16061 | 20.31 | 41.3 | 1.18616 | 23.04 |
| 31.4 | 1.13642 | 17.62 | 36.4 | 1.16111 | 20.37 | 41.4 | 1.18668 | 23.09 |
| 31.5 | 1.13691 | 17.68 | 36.5 | 1.16162 | 20.42 | 41.5 | 1.18720 | 23.15 |
| 31.6 | 1.13740 | 17.73 | 36.6 | 1.16212 | 20.48 | 41.6 | 1.18772 | 23.20 |
| 31.7 | 1.13788 | 17.79 | 36.7 | 1.16262 | 20.53 | 41.7 | 1.18824 | 23.25 |
| 31.8 | 1.13837 | 17.84 | 36.8 | 1.16313 | 20.59 | 41.8 | 1.18887 | 23.31 |
| 31.9 | 1.13885 | 17.90 | 36.9 | 1.16363 | 20.64 | 41.9 | 1.18929 | 23.36 |
| 32.0 | 1.13934 | 17.95 | 37.0 | 1.16413 | 20.70 | 42.0 | 1.18981 | 23.42 |
| 32.1 | 1.13983 | 18.01 | 37.1 | 1.16464 | 20.75 | 42.1 | 1.19033 | 23.47 |
| 32.2 | 1.14032 | 18.06 | 37.2 | 1.16514 | 20.80 | 42.2 | 1.19086 | 23.52 |
| 32.3 | 1.14081 | 18.12 | 37.3 | 1.16565 | 20.86 | 42.3 | 1.19138 | 23.58 |
| 32.4 | 1.14129 | 18.17 | 37.4 | 1.16616 | 20.91 | 42.4 | 1.19190 | 23.63 |
| 32.5 | 1.14178 | 18.23 | 37.5 | 1.16666 | 20.97 | 42.5 | 1.19243 | 23.69 |
| 32.6 | 1.14227 | 18.28 | 37.6 | 1.16717 | 21.02 | 42.6 | 1.19295 | 23.74 |
| 32.7 | 1.14276 | 18.34 | 37.7 | 1.16768 | 21.08 | 42.7 | 1.19348 | 23.79 |
| 32.8 | 1.14325 | 18.39 | 37.8 | 1.16818 | 21.13 | 42.8 | 1.19400 | 23.85 |
| 32.9 | 1.14374 | 18.45 | 37.9 | 1.16869 | 21.19 | 42.9 | 1.19453 | 23.90 |
| 33.0 | 1.14423 | 18.50 | 38.0 | 1.16920 | 21.24 | 43.0 | 1.19505 | 23.96 |
| 33.1 | 1.14472 | 18.56 | 38.1 | 1.16971 | 21.30 | 43.1 | 1.19558 | 24.01 |
| 33.2 | 1.14521 | 18.61 | 38.2 | 1.17022 | 21.35 | 43.2 | 1.19611 | 24.07 |
| 33.3 | 1.14570 | 18.67 | 38.3 | 1.17072 | 21.40 | 43.3 | 1.19663 | 24.12 |
| 33.4 | 1.14620 | 18.72 | 38.4 | 1.17122 | 21.46 | 43.4 | 1.19716 | 24.17 |
| 33.5 | 1.14669 | 18.78 | 38.5 | 1.17174 | 21.51 | 43.5 | 1.19769 | 24.23 |
| 33.6 | 1.14718 | 18.83 | 38.6 | 1.17225 | 21.57 | 43.6 | 1.19822 | 24.28 |
| 33.7 | 1.14767 | 18.89 | 38.7 | 1.17276 | 21.62 | 43.7 | 1.19875 | 24.34 |
| 33.8 | 1.14817 | 18.94 | 38.8 | 1.17327 | 21.68 | 43.8 | 1.19927 | 24.39 |
| 33.9 | 1.14866 | 19.00 | 38.9 | 1.17379 | 21.73 | 43.9 | 1.19980 | 24.44 |
| 34.0 | 1.14915 | 19.05 | 39.0 | 1.17430 | 21.79 | 44.0 | 1.20033 | 24.50 |
| 34.1 | 1.14965 | 19.11 | 39.1 | 1.17481 | 21.84 | 44.1 | 1.20086 | 24.55 |
| 34.2 | 1.15014 | 19.16 | 39.2 | 1.17532 | 21.90 | 44.2 | 1.20139 | 24.61 |
| 34.3 | 1.15064 | 19.22 | 39.3 | 1.17583 | 21.95 | 44.3 | 1.20192 | 24.66 |
| 34.4 | 1.15113 | 19.27 | 39.4 | 1.17635 | 22.00 | 44.4 | 1.20245 | 24.71 |
| 34.5 | 1.15163 | 19.33 | 39.5 | 1.17686 | 22.06 | 44.5 | 1.20299 | 24.77 |
| 34.6 | 1.15213 | 19.38 | 39.6 | 1.17737 | 22.11 | 44.6 | 1.20352 | 24.82 |
| 34.7 | 1.15262 | 19.44 | 39.7 | 1.17789 | 22.17 | 44.7 | 1.20405 | 24.88 |
| 34.8 | 1.15312 | 19.49 | 39.8 | 1.17840 | 22.22 | 44.8 | 1.20458 | 24.93 |
| 34.9 | 1.15362 | 19.55 | 39.9 | 1.17892 | 22.28 | 44.9 | 1.20512 | 24.98 |

*Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.*—Continued.

| Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. |
|---|---|---|---|---|---|---|---|---|
| 45.0 | 1.20565 | 25.04 | 50.0 | 1.23278 | 27.72 | 55.0 | 1.26086 | 30.37 |
| 45.1 | 1.20618 | 25.09 | 50.1 | 1.23334 | 27.77 | 55.1 | 1.26143 | 30.42 |
| 45.2 | 1.20672 | 25.14 | 50.2 | 1.23389 | 27.82 | 55.2 | 1.26200 | 30.47 |
| 45.3 | 1.20725 | 25.20 | 50.3 | 1.23444 | 27.88 | 55.3 | 1.26257 | 30.53 |
| 45.4 | 1.20779 | 25.25 | 50.4 | 1.23499 | 27.93 | 55.4 | 1.26314 | 30.58 |
| 45.5 | 1.20832 | 25.31 | 50.5 | 1.23555 | 27.98 | 55.5 | 1.26372 | 30.63 |
| 45.6 | 1.20886 | 25.36 | 50.6 | 1.23610 | 28.04 | 55.6 | 1.26429 | 30.68 |
| 45.7 | 1.20939 | 25.41 | 50.7 | 1.23666 | 28.09 | 55.7 | 1.26486 | 30.74 |
| 45.8 | 1.20992 | 25.47 | 50.8 | 1.23721 | 28.14 | 55.8 | 1.26544 | 30.79 |
| 45.9 | 1.21046 | 25.52 | 50.9 | 1.23777 | 28.20 | 55.9 | 1.26601 | 30.84 |
| 46.0 | 1.21100 | 25.57 | 51.0 | 1.23832 | 28.25 | 56.0 | 1.26658 | 30.89 |
| 46.1 | 1.21154 | 25.63 | 51.1 | 1.23888 | 28.30 | 56.1 | 1.26716 | 30.95 |
| 46.2 | 1.21208 | 25.68 | 51.2 | 1.23943 | 28.36 | 56.2 | 1.26773 | 31.00 |
| 46.3 | 1.21261 | 25.74 | 51.3 | 1.23999 | 28.41 | 56.3 | 1.26831 | 31.05 |
| 46.4 | 1.21315 | 25.79 | 51.4 | 1.24055 | 28.46 | 56.4 | 1.26889 | 31.10 |
| 46.5 | 1.21369 | 25.84 | 51.5 | 1.24111 | 28.51 | 56.5 | 1.26946 | 31.16 |
| 46.6 | 1.21423 | 25.90 | 51.6 | 1.24166 | 28.57 | 56.6 | 1.27004 | 31.21 |
| 46.7 | 1.21477 | 25.95 | 51.7 | 1.24222 | 28.62 | 56.7 | 1.27062 | 31.26 |
| 46.8 | 1.21531 | 26.00 | 51.8 | 1.24278 | 28.67 | 56.8 | 1.27120 | 31.31 |
| 46.9 | 1.21585 | 26.06 | 51.9 | 1.24334 | 28.73 | 56.9 | 1.27177 | 31.37 |
| 47.0 | 1.21639 | 26.11 | 52.0 | 1.24390 | 28.78 | 57.0 | 1.27235 | 31.42 |
| 47.1 | 1.21693 | 26.17 | 52.1 | 1.24446 | 28.83 | 57.1 | 1.27293 | 31.47 |
| 47.2 | 1.21747 | 26.22 | 52.2 | 1.24502 | 28.89 | 57.2 | 1.27351 | 31.52 |
| 47.3 | 1.21802 | 26.27 | 52.3 | 1.24558 | 28.94 | 57.3 | 1.27409 | 31.58 |
| 47.4 | 1.21856 | 26.33 | 52.4 | 1.24614 | 28.99 | 57.4 | 1.27467 | 31.63 |
| 47.5 | 1.21910 | 26.38 | 52.5 | 1.24670 | 29.05 | 57.5 | 1.27525 | 31.68 |
| 47.6 | 1.21964 | 26.43 | 52.6 | 1.24726 | 29.10 | 57.6 | 1.27583 | 31.73 |
| 47.7 | 1.22019 | 26.49 | 52.7 | 1.24782 | 29.15 | 57.7 | 1.27641 | 31.79 |
| 47.8 | 1.22073 | 26.54 | 52.8 | 1.24839 | 29.20 | 57.8 | 1.27699 | 31.84 |
| 47.9 | 1.22127 | 26.59 | 52.9 | 1.24895 | 29.26 | 57.9 | 1.27758 | 31.89 |
| 48.0 | 1.22182 | 26.65 | 53.0 | 1.24951 | 29.31 | 58.0 | 1.27816 | 31.94 |
| 48.1 | 1.22236 | 26.70 | 53.1 | 1.25008 | 29.36 | 58.1 | 1.27874 | 32.00 |
| 48.2 | 1.22291 | 26.75 | 53.2 | 1.25064 | 29.42 | 58.2 | 1.27932 | 32.05 |
| 48.3 | 1.22345 | 26.81 | 53.3 | 1.25120 | 29.47 | 58.3 | 1.27991 | 32.10 |
| 48.4 | 1.22400 | 26.86 | 53.4 | 1.25177 | 29.52 | 58.4 | 1.28049 | 32.15 |
| 48.5 | 1.22455 | 26.92 | 53.5 | 1.25233 | 29.57 | 58.5 | 1.28107 | 32.20 |
| 48.6 | 1.22509 | 26.97 | 53.6 | 1.25290 | 29.63 | 58.6 | 1.28166 | 32.26 |
| 48.7 | 1.22564 | 27.02 | 53.7 | 1.25347 | 29.68 | 58.7 | 1.28224 | 32.31 |
| 48.8 | 1.22619 | 27.08 | 53.8 | 1.25403 | 29.73 | 58.8 | 1.28283 | 32.36 |
| 48.9 | 1.22673 | 27.13 | 53.9 | 1.25460 | 29.79 | 58.9 | 1.28342 | 32.41 |
| 49.0 | 1.22728 | 27.18 | 54.0 | 1.25517 | 29.84 | 59.0 | 1.28400 | 32.42 |
| 49.1 | 1.22783 | 27.24 | 54.1 | 1.25573 | 29.89 | 59.1 | 1.28459 | 32.52 |
| 49.2 | 1.22838 | 27.29 | 54.2 | 1.25630 | 29.94 | 59.2 | 1.28518 | 32.57 |
| 49.3 | 1.22893 | 27.34 | 54.3 | 1.25687 | 30.00 | 59.3 | 1.28576 | 32.62 |
| 49.4 | 1.22948 | 27.40 | 54.4 | 1.25744 | 30.05 | 59.4 | 1.28635 | 32.67 |
| 49.5 | 1.23003 | 27.45 | 54.5 | 1.25801 | 30.10 | 59.5 | 1.28694 | 32.73 |
| 49.6 | 1.23058 | 27.50 | 54.6 | 1.25857 | 30.16 | 59.6 | 1.28753 | 32.78 |
| 49.7 | 1.23113 | 27.56 | 54.7 | 1.25914 | 30.21 | 59.7 | 1.28812 | 32.83 |
| 49.8 | 1.23168 | 27.61 | 54.8 | 1.25971 | 30.26 | 59.8 | 1.28871 | 32.88 |
| 49.9 | 1.23223 | 27.66 | 54.9 | 1.26028 | 30.31 | 59.9 | 1.28930 | 32.93 |

*Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.*—Continued.

| Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. |
|---|---|---|---|---|---|---|---|---|
| 60.0 | 1.28989 | 32.99 | 65.0 | 1.31989 | 35.57 | 70.0 | 1.35088 | 38.12 |
| 60.1 | 1.29048 | 33.04 | 65.1 | 1.32050 | 35.63 | 70.1 | 1.35155 | 38.18 |
| 60.2 | 1.29107 | 33.09 | 65.2 | 1.32111 | 35.68 | 70.2 | 1.35214 | 38.23 |
| 60.3 | 1.29166 | 33.14 | 65.3 | 1.32172 | 35.73 | 70.3 | 1.35277 | 38.28 |
| 60.4 | 1.29225 | 33.20 | 65.4 | 1.32233 | 35.78 | 70.4 | 1.35340 | 38.33 |
| 60.5 | 1.29284 | 33.25 | 65.5 | 1.32294 | 35.83 | 70.5 | 1.35403 | 38.38 |
| 60.6 | 1.29343 | 33.30 | 65.6 | 1.32355 | 35.88 | 70.6 | 1.35466 | 38.43 |
| 60.7 | 1.29403 | 33.35 | 65.7 | 1.32417 | 35.93 | 70.7 | 1.35530 | 38.48 |
| 60.8 | 1.29462 | 33.40 | 65.8 | 1.32478 | 35.98 | 70.8 | 1.35593 | 38.53 |
| 60.9 | 1.29521 | 33.46 | 65.9 | 1.32539 | 36.04 | 70.9 | 1.35656 | 38.58 |
| 61.0 | 1.29581 | 33.51 | 66.0 | 1.32601 | 36.09 | 71.0 | 1.35720 | 38.63 |
| 61.1 | 1.29646 | 33.56 | 66.1 | 1.32662 | 36.14 | 71.1 | 1.35783 | 38.68 |
| 61.2 | 1.29700 | 33.61 | 66.2 | 1.32724 | 36.19 | 71.2 | 1.35847 | 38.73 |
| 61.3 | 1.29759 | 33.66 | 66.3 | 1.32785 | 36.24 | 71.3 | 1.35910 | 38.78 |
| 61.4 | 1.29819 | 33.71 | 66.4 | 1.32847 | 36.29 | 71.4 | 1.35974 | 38.83 |
| 61.5 | 1.29878 | 33.77 | 66.5 | 1.32908 | 36.34 | 71.5 | 1.36037 | 38.88 |
| 61.6 | 1.29938 | 33.82 | 66.6 | 1.32970 | 36.39 | 71.6 | 1.36101 | 38.93 |
| 61.7 | 1.29998 | 33.87 | 66.7 | 1.33031 | 36.45 | 71.7 | 1.36164 | 38.98 |
| 61.8 | 1.30057 | 33.92 | 66.8 | 1.33093 | 36.50 | 71.8 | 1.36228 | 39.03 |
| 61.9 | 1.30117 | 33.97 | 66.9 | 1.33155 | 36.55 | 71.9 | 1.36292 | 39.08 |
| 62.0 | 1.30177 | 34.03 | 67.0 | 1.33217 | 36.60 | 72.0 | 1.36355 | 39.13 |
| 62.1 | 1.30237 | 34.08 | 67.1 | 1.33278 | 36.65 | 72.1 | 1.36419 | 39.19 |
| 62.2 | 1.30297 | 34.13 | 67.2 | 1.33340 | 36.70 | 72.2 | 1.36483 | 39.24 |
| 62.3 | 1.30356 | 34.18 | 67.3 | 1.33402 | 36.75 | 72.3 | 1.36547 | 39.29 |
| 62.4 | 1.30416 | 34.23 | 67.4 | 1.33464 | 36.80 | 72.4 | 1.36611 | 39.34 |
| 62.5 | 1.30476 | 34.28 | 67.5 | 1.33526 | 36.85 | 72.5 | 1.36675 | 39.39 |
| 62.6 | 1.30536 | 34.34 | 67.6 | 1.33588 | 36.90 | 72.6 | 1.36739 | 39.44 |
| 62.7 | 1.30596 | 34.39 | 67.7 | 1.33650 | 36.96 | 72.7 | 1.36803 | 39.49 |
| 62.8 | 1.30657 | 34.44 | 67.8 | 1.33712 | 37.01 | 72.8 | 1.36867 | 39.54 |
| 62.9 | 1.30717 | 34.49 | 67.9 | 1.33774 | 37.06 | 72.9 | 1.36931 | 39.59 |
| 63.0 | 1.30777 | 34.54 | 68.0 | 1.33836 | 37.11 | 73.0 | 1.36995 | 39.64 |
| 63.1 | 1.30837 | 34.59 | 68.1 | 1.33899 | 37.16 | 73.1 | 1.37059 | 39.69 |
| 63.2 | 1.30897 | 34.65 | 68.2 | 1.33961 | 37.21 | 73.2 | 1.37124 | 39.74 |
| 63.3 | 1.30958 | 34.70 | 68.3 | 1.34023 | 37.26 | 73.3 | 1.37188 | 39.79 |
| 63.4 | 1.31018 | 34.75 | 68.4 | 1.34085 | 37.31 | 73.4 | 1.37252 | 39.84 |
| 63.5 | 1.31078 | 34.80 | 68.5 | 1.34148 | 37.36 | 73.5 | 1.37317 | 39.89 |
| 63.6 | 1.31139 | 34.85 | 68.6 | 1.34210 | 37.41 | 73.6 | 1.37381 | 39.94 |
| 63.7 | 1.31199 | 34.90 | 68.7 | 1.34273 | 37.47 | 73.7 | 1.37446 | 39.99 |
| 63.8 | 1.31260 | 34.96 | 68.8 | 1.34335 | 37.52 | 73.8 | 1.37510 | 40.04 |
| 63.9 | 1.31320 | 35.01 | 68.9 | 1.34398 | 37.57 | 73.9 | 1.37575 | 40.09 |
| 64.0 | 1.31381 | 35.06 | 69.0 | 1.34460 | 37.62 | 74.0 | 1.37639 | 40.14 |
| 64.1 | 1.31442 | 35.11 | 69.1 | 1.34523 | 37.67 | 74.1 | 1.37704 | 40.19 |
| 64.2 | 1.31502 | 35.16 | 69.2 | 1.34525 | 37.72 | 74.2 | 1.37768 | 40.24 |
| 64.3 | 1.31563 | 35.21 | 69.3 | 1.34648 | 37.77 | 74.3 | 1.37833 | 40.29 |
| 64.4 | 1.31624 | 35.27 | 69.4 | 1.34711 | 37.82 | 74.4 | 1.37898 | 40.34 |
| 64.5 | 1.31684 | 35.32 | 69.5 | 1.34774 | 37.87 | 74.5 | 1.37962 | 40.39 |
| 64.6 | 1.31745 | 35.37 | 69.6 | 1.34836 | 37.92 | 74.6 | 1.38027 | 40.44 |
| 64.7 | 1.31806 | 35.42 | 69.7 | 1.34899 | 37.97 | 74.7 | 1.38092 | 40.49 |
| 64.8 | 1.31867 | 35.47 | 69.8 | 1.34962 | 38.02 | 74.8 | 1.38157 | 40.54 |
| 64.9 | 1.31928 | 35.52 | 69.9 | 1.35025 | 38.07 | 74.9 | 1.38222 | 40.59 |

*Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.*—Continued.

| Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. |
|---|---|---|---|---|---|---|---|---|
| 75.0 | 1.38287 | 40.64 | 80.0 | 1.41586 | 43.11 | 85.0 | 1.44986 | 45.54 |
| 75.1 | 1.38352 | 40.69 | 80.1 | 1.41653 | 43.61 | 85.1 | 1.45055 | 45.59 |
| 75.2 | 1.38417 | 40.74 | 80.2 | 1.41720 | 43.21 | 85.2 | 1.45124 | 45.64 |
| 75.3 | 1.38482 | 40.79 | 80.3 | 1.41787 | 43.26 | 85.3 | 1.45193 | 45.69 |
| 75.4 | 1.38547 | 40.84 | 80.4 | 1.41854 | 43.31 | 85.4 | 1.45262 | 45.74 |
| 75.5 | 1.38612 | 40.89 | 80.5 | 1.41921 | 43.36 | 85.5 | 1.45331 | 45.78 |
| 75.6 | 1.38677 | 40.94 | 80.6 | 1.41989 | 43.41 | 85.6 | 1.45401 | 45.83 |
| 75.7 | 1.38743 | 40.99 | 80.7 | 1.42056 | 43.45 | 85.7 | 1.45470 | 45.88 |
| 75.8 | 1.38808 | 41.04 | 80.8 | 1.42123 | 43.50 | 85.8 | 1.45539 | 45.93 |
| 75.9 | 1.38873 | 41.09 | 80.9 | 1.42190 | 43.55 | 85.9 | 1.45609 | 45.98 |
| 76.0 | 1.38939 | 41.14 | 81.0 | 1.42258 | 43.60 | 86.0 | 1.45678 | 46.02 |
| 76.1 | 1.39004 | 41.19 | 81.1 | 1.42325 | 43.65 | 86.1 | 1.45748 | 46.07 |
| 76.2 | 1.39070 | 41.24 | 81.2 | 1.42393 | 43.70 | 86.2 | 1.45817 | 46.12 |
| 76.3 | 1.39135 | 41.29 | 81.3 | 1.42460 | 43.75 | 86.3 | 1.45887 | 46.17 |
| 76.4 | 1.39201 | 41.33 | 81.4 | 1.42528 | 43.80 | 86.4 | 1.45956 | 46.22 |
| 76.5 | 1.39266 | 41.38 | 81.5 | 1.42595 | 43.85 | 86.5 | 1.46026 | 46.26 |
| 76.6 | 1.39332 | 41.43 | 81.6 | 1.42663 | 43.89 | 86.6 | 1.46095 | 46.31 |
| 76.7 | 1.39397 | 41.48 | 81.7 | 1.42731 | 43.94 | 86.7 | 1.46165 | 46.36 |
| 76.8 | 1.39463 | 41.53 | 81.8 | 1.42798 | 43.99 | 86.8 | 1.46235 | 46.41 |
| 76.9 | 1.39529 | 41.58 | 81.9 | 1.42866 | 44.04 | 86.9 | 1.46304 | 46.46 |
| 77.0 | 1.39595 | 41.63 | 82.0 | 1.42934 | 44.09 | 87.0 | 1.46374 | 46.50 |
| 77.1 | 1.39660 | 41.68 | 82.1 | 1.43002 | 44.14 | 87.1 | 1.46444 | 46.55 |
| 77.2 | 1.39726 | 41.73 | 82.2 | 1.43070 | 44.19 | 87.2 | 1.46514 | 46.60 |
| 77.3 | 1.39792 | 41.78 | 82.3 | 1.43137 | 44.24 | 87.3 | 1.46584 | 46.65 |
| 77.4 | 1.39858 | 41.83 | 82.4 | 1.43205 | 44.28 | 87.4 | 1.46654 | 46.69 |
| 77.5 | 1.39924 | 41.88 | 82.5 | 1.43273 | 44.33 | 87.5 | 1.46724 | 46.74 |
| 77.6 | 1.39990 | 41.93 | 82.6 | 1.43341 | 44.38 | 87.6 | 1.46794 | 46.79 |
| 77.7 | 1.40056 | 41.98 | 82.7 | 1.43409 | 44.43 | 87.7 | 1.46864 | 46.84 |
| 77.8 | 1.40122 | 42.03 | 82.8 | 1.43478 | 44.48 | 87.8 | 1.46934 | 46.88 |
| 77.9 | 1.40188 | 42.08 | 82.9 | 1.43546 | 44.53 | 87.9 | 1.47004 | 46.93 |
| 78.0 | 1.40254 | 42.13 | 83.0 | 1.43614 | 44.58 | 88.0 | 1.47074 | 46.98 |
| 78.1 | 1.40321 | 42.18 | 83.1 | 1.43682 | 44.62 | 88.1 | 1.47145 | 47.03 |
| 78.2 | 1.40387 | 42.23 | 83.2 | 1.43750 | 44.67 | 88.2 | 1.47215 | 47.08 |
| 78.3 | 1.40453 | 42.28 | 83.3 | 1.43819 | 44.72 | 88.3 | 1.47285 | 47.12 |
| 78.4 | 1.40520 | 42.32 | 83.4 | 1.43887 | 44.77 | 88.4 | 1.47356 | 47.17 |
| 78.5 | 1.40586 | 42.37 | 83.5 | 1.43955 | 44.82 | 88.5 | 1.47426 | 47.22 |
| 78.6 | 1.40652 | 42.42 | 83.6 | 1.44024 | 44.87 | 88.6 | 1.47496 | 47.27 |
| 78.7 | 1.40719 | 42.47 | 83.7 | 1.44092 | 44.91 | 88.7 | 1.47567 | 47.31 |
| 78.8 | 1.40785 | 42.52 | 83.8 | 1.44161 | 44.96 | 88.8 | 1.47637 | 47.36 |
| 78.9 | 1.40852 | 42.57 | 83.9 | 1.44229 | 45.01 | 88.9 | 1.47708 | 47.41 |
| 79.0 | 1.40918 | 42.62 | 84.0 | 1.44298 | 45.06 | 89.0 | 1.47778 | 47.46 |
| 79.1 | 1.40985 | 42.67 | 84.1 | 1.44367 | 45.11 | 89.1 | 1.47849 | 47.50 |
| 79.2 | 1.41052 | 42.72 | 84.2 | 1.44435 | 45.16 | 89.2 | 1.47920 | 47.55 |
| 79.3 | 1.41118 | 42.77 | 84.3 | 1.44504 | 45.21 | 89.3 | 1.47991 | 47.60 |
| 79.4 | 1.41185 | 42.82 | 84.4 | 1.44573 | 45.25 | 89.4 | 1.48061 | 47.65 |
| 79.5 | 1.41252 | 42.87 | 84.5 | 1.44641 | 45.30 | 89.5 | 1.48132 | 47.69 |
| 79.6 | 1.41318 | 42.92 | 84.6 | 1.44710 | 45.35 | 89.6 | 1.48203 | 47.74 |
| 79.7 | 1.41385 | 42.96 | 84.7 | 1.44779 | 45.40 | 89.7 | 1.48274 | 47.79 |
| 79.8 | 1.41452 | 43.01 | 84.8 | 1.44848 | 45.45 | 89.8 | 1.48345 | 47.83 |
| 79.9 | 1.41519 | 43.06 | 84.9 | 1.44917 | 45.49 | 89.9 | 1.48416 | 47.88 |

*Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.*—Continued.

| Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. | Percentage of sugar according to Balling or degree Brix. | Specific gravity. | Degree Baumé. |
|---|---|---|---|---|---|---|---|---|
| 90.0 | 1.48486 | 47.93 | 94.0 | 1.51359 | 49.81 | 98.0 | 1.54290 | 51.65 |
| 90.1 | 1.48558 | 47.98 | 94.1 | 1.51431 | 49.85 | 98.1 | 1.54365 | 51.70 |
| 90.2 | 1.48629 | 48.02 | 94.2 | 1.51504 | 49.90 | 98.2 | 1.54440 | 51.74 |
| 90.3 | 1.48700 | 48.07 | 94.3 | 1.51577 | 49.94 | 98.3 | 1.54515 | 51.79 |
| 90.4 | 1.48771 | 48.12 | 94.4 | 1.51649 | 49.99 | 98.4 | 1.54590 | 51.83 |
| 90.5 | 1.48842 | 48.17 | 94.5 | 1.51722 | 50.04 | 98.5 | 1.54665 | 51.88 |
| 90.6 | 1.48913 | 48.21 | 94.6 | 1.51795 | 50.08 | 98.6 | 1.54740 | 51.92 |
| 90.7 | 1.48985 | 48.26 | 94.7 | 1.51868 | 50.13 | 98.7 | 1.54815 | 51.97 |
| 90.8 | 1.49056 | 48.31 | 94.8 | 1.51941 | 50.18 | 98.8 | 1.54890 | 52.01 |
| 90.9 | 1.49127 | 48.35 | 94.9 | 1.52014 | 50.22 | 98.9 | 1.54965 | 52.06 |
| 91.0 | 1.49199 | 48.40 | 95.0 | 1.52087 | 50.27 | 99.0 | 1.55040 | 52.11 |
| 91.1 | 1.49270 | 48.45 | 95.1 | 1.52159 | 50.32 | 99.1 | 1.55115 | 52.15 |
| 91.2 | 1.49342 | 48.50 | 95.2 | 1.52232 | 50.36 | 99.2 | 1.55189 | 52.20 |
| 91.3 | 1.49413 | 48.54 | 95.3 | 1.52304 | 50.41 | 99.3 | 1.55264 | 52.24 |
| 91.4 | 1.49485 | 48.59 | 95.4 | 1.52376 | 50.45 | 99.4 | 1.55338 | 52.29 |
| 91.5 | 1.49556 | 48.64 | 95.5 | 1.52449 | 50.50 | 99.5 | 1.55413 | 52.33 |
| 91.6 | 1.49628 | 48.68 | 95.6 | 1.52521 | 50.55 | 99.6 | 1.55487 | 52.38 |
| 91.7 | 1.49700 | 48.73 | 95.7 | 1.52593 | 50.59 | 99.7 | 1.55562 | 52.42 |
| 91.8 | 1.49771 | 48.78 | 95.8 | 1.52665 | 50.64 | 99.8 | 1.55636 | 52.47 |
| 91.9 | 1.49843 | 48.82 | 95.9 | 1.52738 | 50.69 | 99.9 | 1.55711 | 52.51 |
| 92.0 | 1.49915 | 48.87 | 96.0 | 1.52810 | 50.73 | 100.0 | 1.55785 | 52.56 |
| 92.1 | 1.49987 | 48.92 | 96.1 | 1.52884 | 50.78 | | | |
| 92.2 | 1.50058 | 48.96 | 96.2 | 1.52958 | 50.82 | | | |
| 92.3 | 1.50130 | 49.01 | 96.3 | 1.53032 | 50.87 | | | |
| 92.4 | 1.50202 | 49.06 | 96.4 | 1.53106 | 50.92 | | | |
| 92.5 | 1.50274 | 49.11 | 96.5 | 1.53180 | 50.96 | | | |
| 92.6 | 1.50346 | 49.15 | 96.6 | 1.53254 | 51.01 | | | |
| 92.7 | 1.50419 | 49.20 | 96.7 | 1.53328 | 51.05 | | | |
| 92.8 | 1.50491 | 49.25 | 96.8 | 1.53402 | 51.10 | | | |
| 92.9 | 1.50563 | 49.29 | 96.9 | 1.53476 | 51.15 | | | |
| 93.0 | 1.50633 | 49.34 | 97.0 | 1.53550 | 51.19 | | | |
| 93.1 | 1.50707 | 49.39 | 97.1 | 1.53624 | 51.24 | | | |
| 93.2 | 1.50779 | 49.43 | 97.2 | 1.53698 | 51.28 | | | |
| 93.3 | 1.50852 | 49.48 | 97.3 | 1.53772 | 51.33 | | | |
| 93.4 | 1.50924 | 49.53 | 97.4 | 1.53846 | 51.38 | | | |
| 93.5 | 1.50996 | 49.57 | 97.5 | 1.53920 | 51.42 | | | |
| 93.6 | 1.51069 | 49.62 | 97.6 | 1.53994 | 51.47 | | | |
| 93.7 | 1.51141 | 49.67 | 97.7 | 1.54068 | 51.51 | | | |
| 93.8 | 1.51214 | 49.71 | 97.8 | 1.54142 | 51.56 | | | |
| 93.9 | 1.51286 | 49.76 | 97.9 | 1.54216 | 51.60 | | | |

## IV. Alcohol Tables.

*Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.*

| Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. |
|---|---|---|---|---|---|---|---|---|
| **1.0000** | **0.00** | **0.00** | | | | | | |
| **0.9999** | **0.05** | **0.07** | **0.9949** | **2.89** | **3.62** | **0.9899** | **5.94** | **7.40** |
| 8 | 0.11 | 0.13 | 8 | 2.94 | 3.69 | 8 | 6.00 | 7.48 |
| 7 | 0.16 | 0.20 | 7 | 3.00 | 3.76 | 7 | 6.07 | 7.57 |
| 6 | 0.21 | 0.26 | 6 | 3.06 | 3.83 | 6 | 6.14 | 7.66 |
| 5 | 0.26 | 0.33 | 5 | 3.12 | 3.90 | 5 | 6.21 | 7.74 |
| 4 | 0.32 | 0.40 | 4 | 3.18 | 3.98 | 4 | 6.28 | 7.83 |
| 3 | 0.37 | 0.46 | 3 | 3.24 | 4.05 | 3 | 6.36 | 7.92 |
| 2 | 0.42 | 0.53 | 2 | 3.29 | 4.12 | 2 | 6.43 | 8.01 |
| 1 | 0.47 | 0.60 | 1 | 3.35 | 4.20 | 1 | 6.50 | 8.10 |
| 0 | 0.53 | 0.66 | 0 | 3.41 | 4.27 | 0 | 6.57 | 8.18 |
| **0.9989** | **0.58** | **0.73** | **0.9939** | **3.47** | **4.34** | **0.9889** | **6.64** | **8.27** |
| 8 | 0.63 | 0.79 | 8 | 3.53 | 4.42 | 8 | 6.71 | 8.36 |
| 7 | 0.68 | 0.86 | 7 | 3.59 | 4.49 | 7 | 6.78 | 8.45 |
| 6 | 0.74 | 0.93 | 6 | 3.65 | 4.56 | 6 | 6.86 | 8.54 |
| 5 | 0.79 | 0.99 | 5 | 3.71 | 4.63 | 5 | 6.93 | 8.63 |
| 4 | 0.84 | 1.06 | 4 | 3.76 | 4.71 | 4 | 7.00 | 8.72 |
| 3 | 0.89 | 1.13 | 3 | 3.82 | 4.78 | 3 | 7.07 | 8.80 |
| 2 | 0.95 | 1.19 | 2 | 3.88 | 4.85 | 2 | 7.13 | 8.88 |
| 1 | 1.00 | 1.26 | 1 | 3.94 | 4.93 | 1 | 7.20 | 8.96 |
| 0 | 1.06 | 1.34 | 0 | 4.00 | 5.00 | 0 | 7.27 | 9.04 |
| **0.9979** | **1.12** | **1.42** | **0.9929** | **4.06** | **5.08** | **0.9879** | **7.33** | **9.13** |
| 8 | 1.19 | 1.49 | 8 | 4.12 | 5.16 | 8 | 7.40 | 9.21 |
| 7 | 1.25 | 1.57 | 7 | 4.19 | 5.24 | 7 | 7.47 | 9.29 |
| 6 | 1.31 | 1.65 | 6 | 4.25 | 5.32 | 6 | 7.53 | 9.37 |
| 5 | 1.37 | 1.73 | 5 | 4.31 | 5.39 | 5 | 7.60 | 9.45 |
| 4 | 1.44 | 1.81 | 4 | 4.37 | 5.47 | 4 | 7.67 | 9.54 |
| 3 | 1.50 | 1.88 | 3 | 4.44 | 5.55 | 3 | 7.73 | 9.62 |
| 2 | 1.56 | 1.96 | 2 | 4.50 | 5.63 | 2 | 7.80 | 9.70 |
| 1 | 1.62 | 2.04 | 1 | 4.56 | 5.71 | 1 | 7.87 | 9.78 |
| 0 | 1.69 | 2.12 | 0 | 4.62 | 5.78 | 0 | 7.93 | 9.86 |
| **0.9969** | **1.75** | **2.20** | **0.9919** | **4.69** | **5.86** | **0.9869** | **8.00** | **9.95** |
| 8 | 1.81 | 2.27 | 8 | 4.75 | 5.94 | 8 | 8.07 | 10.03 |
| 7 | 1.87 | 2.35 | 7 | 4.81 | 6.02 | 7 | 8.14 | 10.12 |
| 6 | 1.94 | 2.43 | 6 | 4.87 | 6.10 | 6 | 8.21 | 10.21 |
| 5 | 2.00 | 2.51 | 5 | 4.94 | 6.17 | 5 | 8.29 | 10.30 |
| 4 | 2.06 | 2.58 | 4 | 5.00 | 6.24 | 4 | 8.36 | 10.38 |
| 3 | 2.11 | 2.62 | 3 | 5.06 | 6.32 | 3 | 8.43 | 10.47 |
| 2 | 2.17 | 2.72 | 2 | 5.12 | 6.40 | 2 | 8.50 | 10.56 |
| 1 | 2.22 | 2.79 | 1 | 5.19 | 6.48 | 1 | 8.57 | 10.65 |
| 0 | 2.28 | 2.86 | 0 | 5.25 | 6.55 | 0 | 8.64 | 10.73 |
| **0.9959** | **2.33** | **2.93** | **0.9909** | **5.31** | **6.63** | **0.9859** | **8.71** | **10.82** |
| 8 | 2.39 | 3.00 | 8 | 5.37 | 6.71 | 8 | 8.79 | 10.91 |
| 7 | 2.44 | 3.07 | 7 | 5.44 | 6.78 | 7 | 8.86 | 11.00 |
| 6 | 2.50 | 3.14 | 6 | 5.50 | 6.86 | 6 | 8.93 | 11.08 |
| 5 | 2.56 | 3.21 | 5 | 5.56 | 6.94 | 5 | 9.00 | 11.17 |
| 4 | 2.61 | 3.28 | 4 | 5.62 | 7.01 | 4 | 9.07 | 11.26 |
| 3 | 2.67 | 3.35 | 3 | 5.69 | 7.09 | 3 | 9.14 | 11.35 |
| 2 | 2.72 | 3.42 | 2 | 5.75 | 7.17 | 2 | 9.21 | 11.44 |
| 1 | 2.78 | 3.49 | 1 | 5.81 | 7.25 | 1 | 9.29 | 11.52 |
| 0 | 2.83 | 3.55 | 0 | 5.87 | 7.32 | 0 | 9.36 | 11.61 |

*Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.*—Continued.

| Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. |
|---|---|---|---|---|---|---|---|---|
| **0.9849** | **9.43** | **11.70** | **0.9799** | **13.23** | **16.33** | **0.9749** | **17.33** | **21.29** |
| 8 | 9.50 | 11.79 | 8 | 13.31 | 16.43 | 8 | 17.42 | 21.39 |
| 7 | 9.57 | 11.87 | 7 | 13.38 | 16.52 | 7 | 17.50 | 21.49 |
| 6 | 9.64 | 11.96 | 6 | 13.46 | 16.61 | 6 | 17.58 | 21.59 |
| 5 | 9.71 | 12.05 | 5 | 13.54 | 16.70 | 5 | 17.67 | 21.69 |
| 4 | 9.79 | 12.13 | 4 | 13.62 | 16.80 | 4 | 17.75 | 21.79 |
| 3 | 9.86 | 12.22 | 3 | 13.69 | 16.89 | 3 | 17.83 | 21.89 |
| 2 | 9.93 | 12.31 | 2 | 13.77 | 16.98 | 2 | 17.92 | 21.99 |
| 1 | 10.00 | 12.40 | 1 | 13.85 | 17.08 | 1 | 18.00 | 22.09 |
| 0 | 10.08 | 12.49 | 0 | 13.92 | 17.17 | 0 | 18.08 | 22.18 |
| **0.9839** | **10.15** | **12.58** | **0.9789** | **14.00** | **17.26** | **0.9739** | **18.15** | **22.27** |
| 8 | 10.23 | 12.68 | 8 | 14.09 | 17.37 | 8 | 18.23 | 22.36 |
| 7 | 10.31 | 12.77 | 7 | 14.18 | 17.48 | 7 | 18.31 | 22.46 |
| 6 | 10.38 | 12.87 | 6 | 14.27 | 17.59 | 6 | 18.38 | 22.[illegible]5 |
| 5 | 10.46 | 12.96 | 5 | 14.36 | 17.70 | 5 | 18.46 | 22.64 |
| 4 | 10.54 | 13.05 | 4 | 14.45 | 17.81 | 4 | 18.54 | 22.73 |
| 3 | 10.62 | 13.15 | 3 | 14.55 | 17.92 | 3 | 18.62 | 22.82 |
| 2 | 10.69 | 13.24 | 2 | 14.64 | 18.03 | 2 | 18.69 | 22.92 |
| 1 | 10.77 | 13.34 | 1 | 14.73 | 18.14 | 1 | 18.77 | 23.01 |
| 0 | 10.85 | 13.43 | 0 | 14.82 | 18.25 | 0 | 18.85 | 23.10 |
| **0.9829** | **10.92** | **13.52** | **0.9779** | **14.90** | **18.36** | **0.9729** | **18.92** | **23.19** |
| 8 | 11.00 | 13.62 | 8 | 15.00 | 18.48 | 8 | 19.00 | 23.28 |
| 7 | 11.08 | 13.71 | 7 | 15.08 | 18.58 | 7 | 19.08 | 23.38 |
| 6 | 11.15 | 13.81 | 6 | 15.17 | 18.68 | 6 | 19.17 | 23.48 |
| 5 | 11.23 | 13.90 | 5 | 15.25 | 18.78 | 5 | 19.25 | 23.58 |
| 4 | 11.31 | 13.99 | 4 | 15.33 | 18.88 | 4 | 19.33 | 23.68 |
| 3 | 11.38 | 14.09 | 3 | 15.42 | 18.98 | 3 | 19.42 | 23.78 |
| 2 | 11.46 | 14.18 | 2 | 15.50 | 19.08 | 2 | 19.50 | 23.88 |
| 1 | 11.54 | 14.27 | 1 | 15.58 | 19.18 | 1 | 19.58 | 23.98 |
| 0 | 11.62 | 14.37 | 0 | 15.67 | 19.28 | 0 | 19.67 | 24.08 |
| **0.9819** | **11.69** | **14.46** | **0.9769** | **15.75** | **19.39** | **0.9719** | **19.75** | **24.18** |
| 8 | 11.77 | 14.56 | 8 | 15.83 | 19.49 | 8 | 19.83 | 24.28 |
| 7 | 11.85 | 14.65 | 7 | 15.92 | 19.59 | 7 | 19.92 | 24.38 |
| 6 | 11.92 | 14.74 | 6 | 16.00 | 19.68 | 6 | 20.00 | 24.48 |
| 5 | 12.00 | 14.84 | 5 | 16.08 | 19.78 | 5 | 20.08 | 24.58 |
| 4 | 12.08 | 14.93 | 4 | 16.15 | 19.87 | 4 | 20.17 | 24.68 |
| 3 | 12.15 | 15.02 | 3 | 16.23 | 19.96 | 3 | 20.25 | 24.78 |
| 2 | 12.23 | 15.12 | 2 | 16.31 | 20.06 | 2 | 20.33 | 24.88 |
| 1 | 12.31 | 15.21 | 1 | 16.38 | 20.15 | 1 | 20.42 | 24.98 |
| 0 | 12.38 | 15.30 | 0 | 16.46 | 20.24 | 0 | 20.50 | 25.07 |
| **0.9809** | **12.46** | **15.40** | **0.9759** | **16.54** | **20.33** | **0.9709** | **20.58** | **25.17** |
| 8 | 12.54 | 15.49 | 8 | 16.62 | 20.43 | 8 | 20.67 | 25.27 |
| 7 | 12.62 | 15.58 | 7 | 16.69 | 20.52 | 7 | 20.75 | 25.37 |
| 6 | 12.69 | 15.68 | 6 | 16.77 | 20.61 | 6 | 20.83 | 25.47 |
| 5 | 12.77 | 15.77 | 5 | 16.85 | 20.71 | 5 | 20.92 | 25.57 |
| 4 | 12.85 | 15.86 | 4 | 16.92 | 20.80 | 4 | 21.00 | 25.67 |
| 3 | 12.92 | 15.96 | 3 | 17.00 | 20.89 | 3 | 21.08 | 25.76 |
| 2 | 13.00 | 16.05 | 2 | 17.08 | 20.99 | 2 | 21.15 | 25.86 |
| 1 | 13.08 | 16.15 | 1 | 17.17 | 21.09 | 1 | 21.23 | 25.95 |
| 0 | 13.15 | 16.24 | 0 | 17.25 | 21.19 | 0 | 21.31 | 26.04 |

*Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.*—Continued.

| Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. |
|---|---|---|---|---|---|---|---|---|
| **0.9699** | **21.38** | **26.13** | **0.9649** | **25.21** | **30.65** | **0.9599** | **28.62** | **34.61** |
| 8 | 21.46 | 26.22 | 8 | 25.29 | 30.73 | 8 | 28.69 | 34.69 |
| 7 | 21.54 | 26.31 | 7 | 25.36 | 30.82 | 7 | 28.75 | 34.76 |
| 6 | 21.62 | 26.40 | 6 | 25.43 | 30.90 | 6 | 28.81 | 34.83 |
| 5 | 21.69 | 26.49 | 5 | 25.50 | 30.98 | 5 | 28.87 | 34.90 |
| 4 | 21.77 | 26.58 | 4 | 25.57 | 31.07 | 4 | 28.94 | 34.97 |
| 3 | 21.85 | 26.67 | 3 | 25.64 | 31.15 | 3 | 29.00 | 35.05 |
| 2 | 21.92 | 26.77 | 2 | 25.71 | 31.23 | 2 | 29.07 | 35.12 |
| 1 | 22.00 | 26.86 | 1 | 25.79 | 31.32 | 1 | 29.13 | 35.20 |
| 0 | 22.08 | 26.95 | 0 | 25.86 | 31.40 | 0 | 29.20 | 35.28 |
| **0.9689** | **22.15** | **27.04** | **0.9639** | **25.93** | **31.48** | **0.9589** | **29.27** | **35.35** |
| 8 | 22.23 | 27.13 | 8 | 26.00 | 31.57 | 8 | 29.33 | 35.43 |
| 7 | 22.31 | 27.22 | 7 | 26.07 | 31.65 | 7 | 29.40 | 35.51 |
| 6 | 22.38 | 27.31 | 6 | 26.13 | 31.72 | 6 | 29.47 | 35.58 |
| 5 | 22.46 | 27.40 | 5 | 26.20 | 31.80 | 5 | 29.53 | 35.66 |
| 4 | 22.54 | 27.49 | 4 | 26.27 | 31.88 | 4 | 29.60 | 35.74 |
| 3 | 22.62 | 27.59 | 3 | 26.33 | 31.96 | 3 | 29.67 | 35.81 |
| 2 | 22.69 | 27.68 | 2 | 26.40 | 32.03 | 2 | 29.73 | 35.89 |
| 1 | 22.77 | 27.77 | 1 | 26.47 | 32.11 | 1 | 29.80 | 35.97 |
| 0 | 22.85 | 27.86 | 0 | 26.53 | 32.19 | 0 | 29.87 | 36.04 |
| **0.9679** | **22.92** | **27.95** | **0.9629** | **26.60** | **32.27** | **0.9579** | **29.93** | **36.12** |
| 8 | 23.00 | 28.04 | 8 | 26.67 | 32.34 | 8 | 30.00 | 36.20 |
| 7 | 23.08 | 28.13 | 7 | 26.73 | 32.42 | 7 | 30.06 | 36.26 |
| 6 | 23.15 | 28.22 | 6 | 26.80 | 32.50 | 6 | 30.11 | 36.32 |
| 5 | 23.23 | 28.31 | 5 | 26.87 | 32.58 | 5 | 30.17 | 36.39 |
| 4 | 23.31 | 28.41 | 4 | 26.93 | 32.65 | 4 | 30.22 | 36.45 |
| 3 | 23.38 | 28.50 | 3 | 27.00 | 32.73 | 3 | 30.28 | 36.51 |
| 2 | 23.46 | 28.59 | 2 | 27.07 | 32.81 | 2 | 30.33 | 36.57 |
| 1 | 23.54 | 28.68 | 1 | 27.14 | 32.90 | 1 | 30.39 | 36.64 |
| 0 | 23.62 | 28.77 | 0 | 27.21 | 32.98 | 0 | 30.44 | 36.70 |
| **0.9669** | **23.69** | **28.86** | **0.9619** | **27.29** | **33.06** | **0.9569** | **30.50** | **36.76** |
| 8 | 23.77 | 28.95 | 8 | 27.36 | 33.15 | 8 | 30.56 | 36.83 |
| 7 | 23.85 | 29.04 | 7 | 27.43 | 33.23 | 7 | 30.61 | 36.89 |
| 6 | 23.92 | 29.13 | 6 | 27.50 | 33.31 | 6 | 30.67 | 36.95 |
| 5 | 24.00 | 29.22 | 5 | 27.57 | 33.39 | 5 | 30.72 | 37.02 |
| 4 | 24.08 | 29.31 | 4 | 27.64 | 33.48 | 4 | 30.78 | 37.08 |
| 3 | 24.15 | 29.40 | 3 | 27.71 | 33.56 | 3 | 30.83 | 37.14 |
| 2 | 24.23 | 29.49 | 2 | 27.79 | 33.64 | 2 | 30.89 | 37.20 |
| 1 | 24.31 | 29.58 | 1 | 27.86 | 33.73 | 1 | 30.94 | 37.27 |
| 0 | 24.38 | 29.67 | 0 | 27.93 | 33.81 | 0 | 31.00 | 37.34 |
| **0.9659** | **24.46** | **29.76** | **0.9609** | **28.00** | **33.89** | **0.9559** | **31.06** | **37.41** |
| 8 | 24.54 | 29.86 | 8 | 28.06 | 33.97 | 8 | 31.12 | 37.48 |
| 7 | 24.62 | 29.95 | 7 | 28.12 | 34.04 | 7 | 31.19 | 37.55 |
| 6 | 24.69 | 30.04 | 6 | 28.19 | 34.11 | 6 | 31.25 | 37.62 |
| 5 | 24.77 | 30.13 | 5 | 28.25 | 34.18 | 5 | 31.31 | 37.69 |
| 4 | 24.85 | 30.22 | 4 | 28.31 | 34.25 | 4 | 31.37 | 37.76 |
| 3 | 24.92 | 30.31 | 3 | 28.37 | 34.33 | 3 | 31.44 | 37.83 |
| 2 | 25.00 | 30.40 | 2 | 28.44 | 34.40 | 2 | 31.50 | 37.90 |
| 1 | 25.07 | 30.48 | 1 | 28.50 | 34.47 | 1 | 31.56 | 37.97 |
| 0 | 25.14 | 30.57 | 0 | 28.56 | 34.54 | 0 | 31.62 | 38.04 |

*Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.*—Continued.

| Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. |
|---|---|---|---|---|---|---|---|---|
| **0.9549** | **31.69** | **38.11** | **0.9499** | **34.57** | **41.37** | **0.9449** | **37.17** | **44.24** |
| 8 | 31.75 | 38.18 | 8 | 34.62 | 41.42 | 8 | 37.22 | 44.30 |
| 7 | 31.81 | 38.25 | 7 | 34.67 | 41.48 | 7 | 37.28 | 44.36 |
| 6 | 31.87 | 38.33 | 6 | 34.71 | 41.53 | 6 | 37.33 | 44.43 |
| 5 | 31.94 | 38.40 | 5 | 34.76 | 41.58 | 5 | 37.39 | 44.49 |
| 4 | 32.00 | 38.47 | 4 | 34.81 | 41.63 | 4 | 37.44 | 44.55 |
| 3 | 32.06 | 38.53 | 3 | 34.86 | 41.69 | 3 | 37.50 | 44.61 |
| 2 | 32.12 | 38.60 | 2 | 34.90 | 41.74 | 2 | 37.56 | 44.67 |
| 1 | 32.19 | 38.68 | 1 | 34.95 | 41.79 | 1 | 37.61 | 44.73 |
| 0 | 32.25 | 38.75 | 0 | 35.00 | 41.84 | 0 | 37.67 | 44.79 |
| **0.9539** | **32.31** | **38.82** | **0.9489** | **35.05** | **41.90** | **0.9439** | **37.72** | **44.86** |
| 8 | 32.37 | 38.89 | 8 | 35.10 | 41.95 | 8 | 37.78 | 44.92 |
| 7 | 32.44 | 38.96 | 7 | 35.15 | 42.01 | 7 | 37.83 | 44.98 |
| 6 | 32.50 | 39.04 | 6 | 35.20 | 42.06 | 6 | 37.89 | 45.04 |
| 5 | 32.56 | 39.11 | 5 | 35.25 | 42.12 | 5 | 37.94 | 45.10 |
| 4 | 32.62 | 39.18 | 4 | 35.30 | 42.17 | 4 | 38.00 | 45.16 |
| 3 | 32.69 | 39.25 | 3 | 35.35 | 42.23 | 3 | 38.06 | 45.22 |
| 2 | 32.75 | 39.32 | 2 | 35.40 | 42.29 | 2 | 38.11 | 45.28 |
| 1 | 32.81 | 39.40 | 1 | 35.45 | 42.34 | 1 | 38.17 | 45.34 |
| 0 | 32.87 | 39.47 | 0 | 35.50 | 42.40 | 0 | 38.22 | 45.41 |
| **0.9529** | **32.94** | **39.54** | **0.9479** | **35.55** | **42.45** | **0.9429** | **38.28** | **45.47** |
| 8 | 33.00 | 39.61 | 8 | 35.60 | 42.51 | 8 | 38.33 | 45.53 |
| 7 | 33.06 | 39.68 | 7 | 35.65 | 42.56 | 7 | 38.39 | 45.59 |
| 6 | 33.12 | 39.74 | 6 | 35.70 | 42.62 | 6 | 38.44 | 45.65 |
| 5 | 33.18 | 39.81 | 5 | 35.75 | 42.67 | 5 | 38.50 | 45.71 |
| 4 | 33.24 | 39.87 | 4 | 35.80 | 42.73 | 4 | 38.56 | 45.77 |
| 3 | 33.29 | 39.94 | 3 | 35.85 | 42.78 | 3 | 38.61 | 45.83 |
| 2 | 33.35 | 40.01 | 2 | 35.90 | 42.84 | 2 | 38.67 | 45.89 |
| 1 | 33.41 | 40.07 | 1 | 35.95 | 42.89 | 1 | 38.72 | 45.95 |
| 0 | 33.47 | 40.14 | 0 | 36.00 | 42.95 | 0 | 38.78 | 46.02 |
| **0.9519** | **33.53** | **40.20** | **0.9469** | **36.06** | **43.01** | **0.9419** | **38.83** | **46.08** |
| 8 | 33.59 | 40.27 | 8 | 36.11 | 43.07 | 8 | 38.89 | 46.14 |
| 7 | 33.65 | 40.34 | 7 | 36.17 | 43.13 | 7 | 38.94 | 46.20 |
| 6 | 33.71 | 40.40 | 6 | 36.22 | 43.19 | 6 | 39.00 | 46.26 |
| 5 | 33.76 | 40.47 | 5 | 36.28 | 43.26 | 5 | 39.05 | 46.32 |
| 4 | 33.82 | 40.53 | 4 | 36.33 | 43.32 | 4 | 39.10 | 46.37 |
| 3 | 33.88 | 40.60 | 3 | 36.39 | 43.38 | 3 | 39.15 | 46.42 |
| 2 | 33.94 | 40.67 | 2 | 36.44 | 43.44 | 2 | 39.20 | 46.48 |
| 1 | 34.00 | 40.74 | 1 | 36.50 | 43.50 | 1 | 39.25 | 46.53 |
| 0 | 34.05 | 40.79 | 0 | 36.56 | 43.56 | 0 | 39.30 | 46.59 |
| **0.9509** | **34.10** | **40.84** | **0.9459** | **36.61** | **43.63** | **0.9409** | **39.35** | **46.64** |
| 8 | 34.14 | 40.90 | 8 | 36.67 | 43.69 | 8 | 39.40 | 46.70 |
| 7 | 34.19 | 40.95 | 7 | 36.72 | 43.75 | 7 | 39.45 | 46.75 |
| 6 | 34.24 | 41.00 | 6 | 36.78 | 43.81 | 6 | 39.50 | 46.80 |
| 5 | 34.29 | 41.05 | 5 | 36.83 | 43.87 | 5 | 39.55 | 46.86 |
| 4 | 34.33 | 41.11 | 4 | 36.89 | 43.93 | 4 | 39.60 | 46.91 |
| 3 | 34.38 | 41.16 | 3 | 36.94 | 44.00 | 3 | 39.65 | 46.97 |
| 2 | 34.43 | 41.21 | 2 | 37.00 | 44.06 | 2 | 39.70 | 47.02 |
| 1 | 34.48 | 41.26 | 1 | 37.06 | 44.12 | 1 | 39.75 | 47.08 |
| 0 | 34.52 | 41.32 | 0 | 37.11 | 44.18 | 0 | 39.80 | 47.13 |

*Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.*—Continued.

| Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. |
|---|---|---|---|---|---|---|---|---|
| **0.9399** | **39.85** | **47.18** | **0.9349** | **42.33** | **49.86** | **0.9299** | **44.68** | **52.34** |
| 8 | 39.90 | 47.24 | 8 | 42.38 | 49.91 | 8 | 44.73 | 52.39 |
| 7 | 39 95 | 47.29 | 7 | 42.43 | 49.96 | 7 | 44.77 | 52.44 |
| 6 | 40.00 | 47.35 | 6 | 42.48 | 50.01 | 6 | 44.82 | 52.48 |
| 5 | 40.05 | 47.40 | 5 | 42.52 | 50.06 | 5 | 44.86 | 52.53 |
| 4 | 40.10 | 47.45 | 4 | 42.57 | 50.11 | 4 | 44.91 | 52.58 |
| 3 | 40.15 | 47.51 | 3 | 42.62 | 50.16 | 3 | 44.96 | 52.63 |
| 2 | 40.20 | 47.56 | 2 | 42.67 | 50.21 | 2 | 45.00 | 52.68 |
| 1 | 40.25 | 47.62 | 1 | 42.71 | 50.26 | 1 | 45.05 | 52.72 |
| 0 | 40.30 | 47.67 | 0 | 42.76 | 50.31 | 0 | 45.09 | 52.77 |
| **0.9389** | **40.35** | **47.72** | **0.9339** | **42.81** | **50.37** | **0.9280** | **45.55** | **53.24** |
| 8 | 40.40 | 47.78 | 8 | 42.86 | 50.42 | 70 | 46.00 | 53.72 |
| 7 | 40.45 | 47.83 | 7 | 42.90 | 50.47 | 60 | 46.46 | 54.19 |
| 6 | 40.50 | 47.89 | 6 | 42.95 | 50.52 | 50 | 46.91 | 54.66 |
| 5 | 40.55 | 47.94 | 5 | 43.00 | 50.57 | 40 | 47.36 | 55.13 |
| 4 | 40.60 | 47.99 | 4 | 43.05 | 50.62 | 30 | 47.82 | 55.60 |
| 3 | 40.65 | 48.05 | 3 | 43.10 | 50.67 | 20 | 48.27 | 56.07 |
| 2 | 40.70 | 48.10 | 2 | 43.14 | 50.72 | 10 | 48.73 | 56.54 |
| 1 | 40.75 | 48.16 | 1 | 43.19 | 50.77 | 00 | 49.16 | 56.98 |
| 0 | 40.80 | 48.21 | 0 | 43.24 | 50.82 | | | |
| **0.9379** | **40.85** | **48.26** | **0.9329** | **43.29** | **50.87** | **0.9190** | **49.64** | **57.45** |
| 8 | 40.90 | 48.32 | 8 | 43.33 | 50.92 | 80 | 50.09 | 57.92 |
| 7 | 40.95 | 48.37 | 7 | 43.39 | 50.97 | 70 | 50.52 | 58.36 |
| 6 | 41.00 | 48.43 | 6 | 43.43 | 51.02 | 60 | 50.96 | 58.80 |
| 5 | 41.05 | 48.48 | 5 | 43.48 | 51.07 | 50 | 51.38 | 59.22 |
| 4 | 41.10 | 48.54 | 4 | 43.52 | 51.12 | 40 | 51.79 | 59.63 |
| 3 | 41.15 | 48.59 | 3 | 43.57 | 51.17 | 30 | 52.23 | 60.07 |
| 2 | 41.20 | 48.64 | 2 | 43.62 | 51.22 | 20 | 52.58 | 60.52 |
| 1 | 41.25 | 48.70 | 1 | 43.67 | 51.27 | 10 | 53.13 | 60.97 |
| 0 | 41.30 | 48.75 | 0 | 43.71 | 51.32 | 00 | 53.57 | 61.40 |
| **0.9369** | **41.35** | **48.80** | **0.9319** | **43.76** | **51.38** | **0.9090** | **54.00** | **61.84** |
| 8 | 41.40 | 48.86 | 8 | 43.81 | 51.43 | 80 | 54.48 | 62.31 |
| 7 | 41.45 | 48.91 | 7 | 43.86 | 51.48 | 70 | 54.95 | 62.79 |
| 6 | 41.50 | 48.97 | 6 | 43.90 | 51.53 | 60 | 55.41 | 63.24 |
| 5 | 41.55 | 49.02 | 5 | 43.95 | 51.58 | 50 | 55.86 | 63.69 |
| 4 | 41.60 | 49.07 | 4 | 44.00 | 51.63 | 40 | 56.32 | 64.14 |
| 3 | 41.65 | 49.13 | 3 | 44.05 | 51.68 | 30 | 56.77 | 64.58 |
| 2 | 41.70 | 49.18 | 2 | 44.09 | 51.72 | 20 | 57.21 | 65.01 |
| 1 | 41.75 | 49.23 | 1 | 44.14 | 51.77 | 10 | 57.63 | 65.41 |
| 0 | 41.80 | 49.29 | 0 | 44.18 | 51.82 | 00 | 58.05 | 65.81 |
| **0.9359** | **41.85** | **49.34** | **0.9309** | **44.23** | **51.87** | **0.8990** | **58.50** | **66.25** |
| 8 | 41.90 | 49.40 | 8 | 44.27 | 51.91 | 80 | 58.95 | 66.69 |
| 7 | 41.95 | 49.45 | 7 | 44.32 | 51.96 | 70 | 59.39 | 67.11 |
| 6 | 42.00 | 49.50 | 6 | 44.36 | 52.01 | 60 | 59.83 | 67.53 |
| 5 | 42.05 | 49.55 | 5 | 44.41 | 52.06 | 50 | 60.26 | 67.93 |
| 4 | 42.10 | 49.61 | 4 | 44.46 | 52.10 | 40 | 60.67 | 68.33 |
| 3 | 42.14 | 49.66 | 3 | 44.50 | 52.15 | 30 | 61.08 | 68.72 |
| 2 | 42.19 | 49.71 | 2 | 44.55 | 52.20 | 20 | 61.50 | 69.11 |
| 1 | 42.24 | 49.76 | 1 | 44.59 | 52.25 | 10 | 61.92 | 69.50 |
| 0 | 42.29 | 49.81 | 0 | 44.64 | 52.29 | 00 | 62.36 | 69.92 |

*Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.*—Continued.

| Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. | Specific gravity at 15.5° C. | Percentage of absolute alcohol by weight. | Percentage of absolute alcohol by volume. |
|---|---|---|---|---|---|---|---|---|
| **0.8890** | **62.82** | **70.35** | 40 | 77.71 | 83.60 | **0.8190** | **91.36** | **94.26** |
| 80 | 63.26 | 70.77 | 30 | 78.12 | 83.94 | 80 | 91.71 | 94.51 |
| 70 | 63.70 | 71.17 | 20 | 78.52 | 84.27 | 70 | 92.07 | 94.76 |
| 60 | 64.13 | 71.58 | 10 | 78.92 | 84.60 | 60 | 92.44 | 95.03 |
| 50 | 64.57 | 71.98 | 00 | 79.32 | 84.93 | 50 | 92.81 | 95.29 |
| 40 | 65.00 | 72.38 | | | | 40 | 93.18 | 95.55 |
| 30 | 65.42 | 72.77 | **0.8490** | **79.72** | **85.26** | 30 | 93.55 | 95.82 |
| 20 | 65.83 | 73.15 | 80 | 80.13 | 85.59 | 20 | 93.92 | 96.08 |
| 10 | 66.26 | 73.54 | 70 | 80.54 | 85.94 | 10 | 94.28 | 96.32 |
| 00 | 66.70 | 73.93 | 60 | 80.96 | 86.28 | 00 | 94.62 | 96.55 |
| | | | 50 | 81.36 | 86.61 | | | |
| **0.8790** | **67.18** | **74.33** | 40 | 81.76 | 86.93 | **0.8090** | **94.97** | **96.78** |
| 80 | 67.54 | 74.70 | 30 | 82.15 | 87.24 | 80 | 95.32 | 97.02 |
| 70 | 67.96 | 75.08 | 20 | 82.54 | 87.55 | 70 | 95.68 | 97.27 |
| 60 | 68.38 | 75.45 | 10 | 82.92 | 87.85 | 60 | 96.03 | 97.51 |
| 50 | 68.79 | 75.83 | 00 | 83.31 | 88.16 | 50 | 96.37 | 97.73 |
| 40 | 69.21 | 76.20 | | | | 40 | 96.70 | 97.94 |
| 30 | 69.63 | 76.57 | **0.8390** | **83.69** | **88.46** | 30 | 97.03 | 98.16 |
| 20 | 70.04 | 76.94 | 80 | 84.08 | 88.76 | 20 | 97.37 | 98.37 |
| 10 | 70.44 | 77.29 | 70 | 84.48 | 89.08 | 10 | 97.70 | 98.59 |
| 00 | 70.84 | 77.64 | 60 | 84.88 | 89.39 | 00 | 98.03 | 98.80 |
| | | | 50 | 85.27 | 89.70 | | | |
| **0.8690** | **71.25** | **78.00** | 40 | 85.65 | 89.99 | **0.7990** | **98.34** | **98.98** |
| 80 | 71.67 | 78.36 | 30 | 86.04 | 90.29 | 80 | 98.66 | 99.16 |
| 70 | 72.09 | 78.73 | 20 | 86.42 | 90.58 | 70 | 98.97 | 99.35 |
| 60 | 72.52 | 79.12 | 10 | 86.81 | 90.88 | 60 | 99.29 | 99.55 |
| 50 | 72.96 | 79.50 | 00 | 87.19 | 91.17 | 50 | 99.61 | 99.75 |
| 40 | 73.38 | 79.86 | | | | 40 | 99.94 | 99.96 |
| 30 | 73.79 | 80.22 | **0.8290** | **87.58** | **91.46** | | | |
| 20 | 74.23 | 80.60 | 80 | 87.96 | 91.75 | **0.7939** | **99.97** | **99.98** |
| 10 | 74.68 | 81.00 | 70 | 88.36 | 92.05 | | Absolute | Alcohol. |
| 00 | 75.14 | 81.40 | 60 | 88.76 | 92.36 | **0.7938** | **100.00** | **100.00** |
| | | | 50 | 89.16 | 92.66 | | | |
| **0.8590** | **75.59** | **81.80** | 40 | 89.54 | 92.94 | | | |
| 80 | 76.04 | 82.19 | 30 | 89.92 | 93.23 | | | |
| 70 | 76.46 | 82.54 | 20 | 90.29 | 93.49 | | | |
| 60 | 76.88 | 82.90 | 10 | 90.64 | 93.75 | | | |
| 50 | 77.29 | 83.25 | 00 | 91.00 | 94.00 | | | |

## V. Physical and Chemical Constants of Fixed Oils and Fats.

(Chiefly from Benedikt-Lewkowitsch.)

| | Specific gravity at 15°. | Specific gravity at 100°. | Melting-point. C. | Solidifying-point. C. |
|---|---|---|---|---|
| Linseed oil | 0.931–0.935 | 0.880 | —16° to —20° | —16° |
| Hemp-seed oil | 0.925–0.931 | ... | ... | —27° |
| Walnut oil | 0.925–0.926 | 0.871 | ... | —27° |
| Poppy-seed oil | 0.924–0.927 | 0.878 | ... | —18° |
| Niger-seed oil | 0.926–0.928 | 0.874 | ... | —9° |
| Sunflower oil | 0.924–0.926 | 0.919 | ... | —17° |
| Fir-seed oil | 0.925–0.928 | ... | ... | —27° to —30° |
| Madia oil | 0.926–0.928 | ... | ... | —11° to —15° |
| Maize oil | 0.921–0.924 | ... | ... | —10° to —15° |
| Cotton-seed oil | 0.922–0.930 | 0.867 | ... | 12° |
| Sesamé oil | 0.923–0.924 | 0.871 | ... | —5° |
| Rape-seed oil | 0.914–0.917 | 0.863 | ... | —2° to —10° |
| Black mustard oil | 0.916–0 920 | ... | ... | —17.5° |
| Croton oil | 0.942–0.955 | ... | ... | —16° |
| Castor oil | 0.960–0.966 | 0.910 | ... | —12° to —18° |
| Apricot kernel oil | 0.915–0.919 | ... | ... | —14° |
| Almond oil | 0.915–0.920 | ... | ... | —10° |
| Earthnut oil | 0.916–0.920 | 0.867 | ... | —3° to —7° |
| Olive oil | 0.914–0.917 | 0.862 | ... | 2° |
| Menhaden oil | 0.927–0.933 | ... | ... | —4° |
| Cod-liver oil | 0.922–0.927 | 0.874 | ... | 0° to —10° |
| Seal oil | 0.924–0.929 | 0.873 | ... | 3° |
| Whale oil | 0.920–0.930 | 0.872 | ... | —2° |
| Dolphin oil | 0.917–0.918 | ... | ... | 5° to —3° |
| Porpoise oil | 0.926 | 0.871 | ... | —16° |
| Neat's-foot oil | 0.914–0.916 | 0.861 | ... | 0° to 1.5° |
| Cotton-seed stearine | 0.919–0.923 | 0.867 | 40° | 31° to 32.5° |
| Palm oil | 0.921–0.925 | 0.856 | 27° to 42° | ... |
| Cacao butter | 0.950–0.952 | 0 858 | 30° to 33° | 25° to 26° |
| Cocoa-nut oil | 0.925–0.926 | 0.873 | 20° to 26° | 16° to 20° |
| Myrtle wax | 0.995 | 0 875 | 40° to 44° | 39° to 43° |
| Japan wax | 0.970–0.980 | 0.875 | 51° to 54.5° | 46° |
| Lard | 0.931–0.938 | 0.861 | 41° to 46° | 29° |
| Bone fat | 0.914–0.916 | ... | 21° to 22° | 15° to 17° |
| Tallow | 0.943–0.952 | 0.860 | 42° to 46° | 35° to 37° |
| Butter fat | 0.927–0.936 | 0.866 | 29.5° to 33° | 19° to 20° |
| Oleomargarine | 0.924–0.930 | 0.859 | ... | ... |
| Sperm oil | 0.875–0.884 | 0.833 | ... | —25° |
| Bottle-nose oil | 0.879–0.880 | 0.827 | ... | ... |
| Carnauba wax | 0.990–0.999 | 0.842 | 84° to 85° | 80° to 81° |
| Wool-fat | 0.973 | 0.901 | 39° to 42° | 30° to 30.2° |
| Beeswax | 0.958–0.969 | 0.822 | 62° to 64° | 60.5° to 62° |
| Spermaceti | 0.960 | 0.812 | 43.5° to 49° | 43.4° to 44.2° |
| Chinese wax | 0.970 | 0.810 | 80.5° to 81° | 80.5° to 81° |

## V. Physical and Chemical Constants of Fixed Oils and Fats.—Continued.

(Chiefly from Benedikt-Lewkowitsch.)

| | Saponification value. | Maumené test. | Iodine value. | Hehner value. | Reichert value. |
|---|---|---|---|---|---|
| Linseed oil | 189-195 | 104°-111° | 170-181 | . . . | . . . |
| Hemp-seed oil | 190-193 | 95°-96° | 148 | . . . | . . . |
| Walnut oil | 194-197 | 96°-101° | 144-147 | . . . | . . . |
| Poppy-seed oil | 193-197 | 86°-88° | 134-141 | 95.38 | . . . |
| Niger-seed oil | 189-191 | 81°-82° | 132.9 | . . . | . . . |
| Sunflower oil | 193-194 | 72°-75° | 120-129 | 95 | . . . |
| Fir-seed oil | 191.3 | 98°-99° | 118.9-120 | . . . | . . . |
| Madia oil | 192.8 | 95°-99° | 117.5-119.5 | . . . | . . . |
| Maize oil | 188-190.4 | 56°-60.5° | 117-122 | 96 | 2.5 |
| Cotton-seed oil | 191-196 | 68°-77° | 104-108 | 96.17 | . . . |
| Sesamé oil | 187-191 | 64°-68° | 105-109 | 95.8 | 0.35 |
| Rape-seed oil | 175-178 | 51°-60° | 99-105 | 95 | . . . |
| Black mustard oil | 174-174.6 | 43°-44° | 106.3 | . . . | . |
| Croton oil | 210.3-215 | . . . . . | 101.7-104 | 89 | 13.5 |
| Castor oil | 178-183 | 46°-47° | 83.4-85.9 | . . . | 1.4 |
| Apricot kernel oil | 192.2-193.1 | 42.5°-46° | 100-101 | . . . | . . . |
| Almond oil | 190.5-195.4 | 51°-53° | 96-99 | 96.2 | . . . |
| Earthnut oil | 190-197 | 45°-49° | 95-98 | 95.86 | . . . |
| Olive oil | 191-196 | 41.5°-45.5° | 81.6-84.5 | 95.43 | 0.3 |
| Menhaden oil | 189.3-192 | 123°-128° | 147.9 | . . . | 1.2 |
| Cod-liver oil | 182-187 | 102°-103° | 139-152 | 95.3 | . . . |
| Seal oil | 190-196 | 92° | 125-130 | 94.2 | 0.22 |
| Whale oil | 188-193 | 91°-92° | 49 | 93.5 | 2.04 |
| Dolphin oil { Body oil | 197.3 | . . . . . | 99.5 | 93.07 | 5.6 |
| Dolphin oil { Jaw oil | 290 | . . | 32.8 | 66.28 | 65.92 |
| Porpoise oil { Body oil | 216-218.8 | 50° | . . . . . | . . . | 23.45 |
| Porpoise oil { Jaw oil | 253.7 | . . . . . | 49.6 | 68.41 | 65.8 |
| Neat's-foot oil | 194.3 | 47°-48.5° | 69.3-70.4 | . . . | . . . |
| Cotton-seed stearine | 194.6-195.1 | 48° | 88.7-92.8 | 96.3 | . . . |
| Palm oil | 196.3-202 | . . . . . | 51-52.4 | 95.6 | 0.5 |
| Cacao butter | 192.2-193.5 | . . . . . | 32-37 | 94.59 | 1.6 |
| Cocoa-nut oil | 250-253 | . . . . . | 8.5-9.3 | 88.6 | 3.7 |
| Myrtle wax | 205.7-211.7 | . . . . . | 10.7 | . . . | . . . |
| Japan wax | 220-222.4 | . . . . . | 4.2-6.6 | . . . | . . . |
| Lard | 195.3-196.6 | 27°-32° | 57-63 | 96 | . . . |
| Bone fat | 190.9 | . . . . . | 46.3-49.6 | . . . | . . |
| Tallow | 195-198 | . . . . . | 36-40 | 95.6 | 0.25 |
| Butter fat | 221.5-227 | . . . . . | 26-35 | 87.5 | 28.78 |
| Oleomargarine | . . . . | . . . . . | 55.3 | 95-96 | 2.6 |
| Sperm oil | 132.5-147 | 47°-51° | 84 | . . . | 1.3 |
| Bottle-nose oil | 126-134 | 41°-47° | 77.4-82 | . . . | 1.4 |
| Carnauba wax | 80-84 | . . . . . | 13.5 | . . . | . . . |
| Wool-fat | 98.2-102.4 | . . . . . | 25-28 | . . . | . . |
| Beeswax | 91-96 | . . . . . | 8.3-11 | . . . | . . . |
| Spermaceti | 128 | . . . . . | . . . . . . | . . . | . . . |
| Chinese wax | 63 | . . . . . | . . . . . . | . . . | . |

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THE END.